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HETEROCYCLES BASED ON GROUP III, IV, AND V ELEMENTS  
PRECURSORS FOR NOVEL GLASSES AND CERAMICS

Contract No. F49620-85-C-0042

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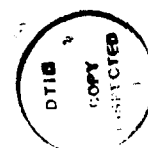
$[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\text{NH}_2)_2]_3\text{Al}$  respectively. The structures of these novel compositions were determined by single crystal X-ray crystallography.  $[(\text{Me}_3\text{Si})_2\text{NAlNH}]_4$  was produced by thermolysis of  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{AlNH}_2]_2$  at  $225^\circ\text{C}$ . Pyrolysis of  $[(\text{Me}_3\text{Si})_2\text{NAlNH}]_4$  both in vacuo and ammonia failed to give pure AlN; silicon and carbon were retained. Thermolysis of  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\text{NH}_2)_2]_3\text{Al}$  at  $200^\circ\text{C}$  resulted in a loss of 5  $\text{HN}(\text{SiMe}_3)_2$ . Further pyrolysis in an inert atmosphere gave  $6\text{AlN}\cdot\text{Si}_3\text{N}_4$ ; AlN was formed in ammonia.

$[(\text{Me}_3\text{Si})_2\text{NAlNSiMe}_3]_2$  was obtained by reacting  $[\text{AlCl}_2\text{NHSiMe}_3]_2$  with  $\text{LiN}(\text{SiMe}_3)_2$ . Exposure to ammonia led to  $\text{Me}_3\text{SiN}-\text{AlNHSiMe}_3-\text{NSiMe}_3-\text{AlNH}_2$  which on reaction with  $(\text{Me}_3\text{Si})_2\text{NB}(\text{Cl})\text{NHSiMe}_3$  and  $\text{NEt}_3$  gave  $\text{Et}_3\text{N}\cdot\text{Cl}_2\text{AlN}(\text{SiMe}_3)\text{B}(\text{NH}_2)\text{NHSiMe}_3$ , a processible precursor to AlN·BN ceramic.

## FOREWORD

This Final Report describes the work performed by the Chemicals and Materials Research department, Ultrasystems, Inc. under Contract F49620-85-C-0042, "Heterocycles Based on Group III, IV, and V Elements. Precursors for Novel Glasses and Ceramics." The investigations were carried out during the period 1 March 1985 to 30 April 1990 by J. H. Nakahara, S. R. Masuda, J. G. Shih, L. A. Hoferkamp, R. H. Kratzer, and K. L. Paciorek, Project Manager. This contract was administered by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, with Dr. Anthony J. Matuszuko as Technical Program Manager.

We acknowledge the contribution of W. R. Schmidt of Rensselaer Polytechnic Institute for providing the XRD and EDS analyses as well as the high temperature pyrolysis studies. We also wish to thank C. George, J. Flippen-Anderson, and R. Gilardi of the Naval Research Laboratory for the X-ray crystal structure determinations.



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## 1. ABSTRACT

Aluminum nitride was prepared by stepwise pyrolysis of aluminum chloride-hexamethyldisilazane adduct via  $[\text{AlCl}_2\text{NHSiMe}_3]_2$ , then  $[\text{AlClNH}]_3\text{AlCl}_2\text{NHSiMe}_3$  and  $(\text{AlClNH})_4$ . Each of the intermediates was characterized. The process lent itself to AlN coatings production.

A series of novel bis(trimethylsilyl)amino-substituted compounds,  $\text{AlCl}_2\text{N}(\text{SiMe}_3)_2 \cdot \text{NEt}_3$ ,  $\text{AlCl}[\text{N}(\text{SiMe}_3)_2]_2$  and  $\text{Al}[\text{N}(\text{SiMe}_3)_2]_3$ , was prepared from  $\text{AlCl}_3 \cdot \text{NEt}_3$  and  $\text{AlCl}_3$  and their reactions studied.  $\text{AlCl}_2\text{N}(\text{SiMe}_3)_2 \cdot \text{NEt}_3$  failed to react with hexamethyldisilazane; no trimethylchlorosilane was eliminated on pyrolysis; pyrolysis of  $\text{AlCl}[\text{N}(\text{SiMe}_3)_2]_2$  gave methane.  $\text{AlCl}[\text{N}(\text{SiMe}_3)_2]_2$  with ammonia at  $0^\circ\text{C}$  gave  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{AlNH}_2]_2$ ; at  $-20^\circ\text{C}$ , a thus far unidentified compound was produced. Reaction of boron trichloride with  $\text{Al}[\text{N}(\text{SiMe}_3)_2]_3$  resulted in trimethylboron formation, some boron incorporation, accompanied by tetramethylsilane elimination and methyl group replacement by chlorine. Treatment of  $\text{Al}[\text{N}(\text{SiMe}_3)_2]_3$  with ammonia in 1:1 and 1:2 mole ratios formed  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{AlNH}_2]_2$  and  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\text{NH}_2)_2]_3\text{Al}$  respectively. The structures of these novel compositions were determined by single crystal X-ray crystallography.  $(\text{Me}_3\text{Si})_2\text{NAlNH}]_4$  was produced by thermolysis of  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{AlNH}_2]_2$  at  $225^\circ\text{C}$ . Pyrolysis of  $(\text{Me}_3\text{Si})_2\text{NAlNH}]_4$  both in vacuo and ammonia failed to give pure AlN; silicon and carbon were retained. Thermolysis of  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\text{NH}_2)_2]_3\text{Al}$



at 200°C resulted in a loss of  $5\text{HN}(\text{SiMe}_3)_2$ . Further pyrolysis in an inert atmosphere gave  $6\text{AlN}\cdot\text{Si}_3\text{N}_4$ ; AlN was formed in ammonia.

The novel 4-membered ring compound,  $[(\text{Me}_3\text{Si})_2\text{NAlNSiMe}_3]_2$  was obtained from the reaction of  $[\text{AlCl}_2\text{NHSiMe}_3]_2$  and  $\text{LiN}(\text{SiMe}_3)_2$ . Exposure to ammonia led to the arrangement  $\text{Me}_3\text{SiN}-\text{AlNHSiMe}_3-\text{NSiMe}_3-\text{AlNH}_2$  which on reaction with  $(\text{Me}_3\text{Si})_2\text{NB}(\text{Cl})\text{NHSiMe}_3$  and  $\text{NEt}_3$  gave  $\text{Et}_3\text{N}\cdot\text{Cl}_2\text{AlN}(\text{SiMe}_3)\text{B}(\text{NH}_2)\text{NHSiMe}_3$ , a processible precursor to AlN·BN ceramic. Attempts at synthesis of other AlN·BN precursors and AlNP systems were largely unsuccessful.

## 2. INTRODUCTION

The general objective of this program was to explore the feasibility of synthesizing novel heterocyclics from the group of elements consisting of B, C, N, Al, Si, and P, the ultimate goal being the production of processible precursors for novel ceramics of unusual properties. The major efforts under the program were devoted to development of processible preceramic systems leading to aluminum nitride and multi-element nitride ceramics.

Aluminum nitride, in view of its high thermal conductivity, among other desirable properties, is of interest in electronic applications, in particular in packaging of electronic microcircuits [Ref. 1]. Having a processible ceramic precursor to a degree determines stoichiometry and simplifies greatly the manufacturing process. The general benefits of preceramic precursors are well known [Ref. 2,3]. For nitride ceramics, such as aluminum nitride and boron nitride, it is of importance to have nitrogen incorporated in the preceramic material and to have substituents which provide for readily formed volatile leaving groups. In aluminum nitride, these aspects have been addressed [Ref. 1,4-7] by ammonolysis of soluble aluminum compounds or by introducing additional nitrogen sources into the molecule, as is exemplified by the dialkylaluminum azide system [Ref. 8].

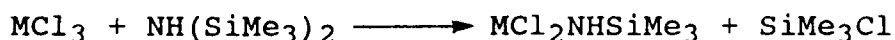
Carbon retention is one of the persistent problems in the transformation of organometallics into carbon-free ceramics [Ref. 3,9]. Absence of metal-carbon bonds minimizes this problem, as was shown by the utilization of trimethylsilylamino

substituents in the boron nitride synthesis [Ref. 10,11]. Therefore, the major emphasis under this program was on the synthesis of novel trimethylsilylamino-substituted aluminum compounds and the study of their reactions. This included investigations of novel Al-N-B-N compositions and the exploration of the interactions of chloro-substituted boron and phosphorus compounds with aluminum compounds.

### 3. RESULTS AND DISCUSSION

#### 3.1 Synthesis and Thermolysis of Aluminum Chloride·Hexamethyldisilazane Adduct

The similarity in the reactivity of aluminum and boron compositions with trimethylsilylamino-compounds was indicated by the work of Becke-Goehring and Krill [Ref. 12] who claimed that both boron trichloride and aluminum chloride, on reaction with hexamethyldisilazane, give the compound  $MCl_2NHSiMe_3$ , M being either boron or aluminum, i.e.,



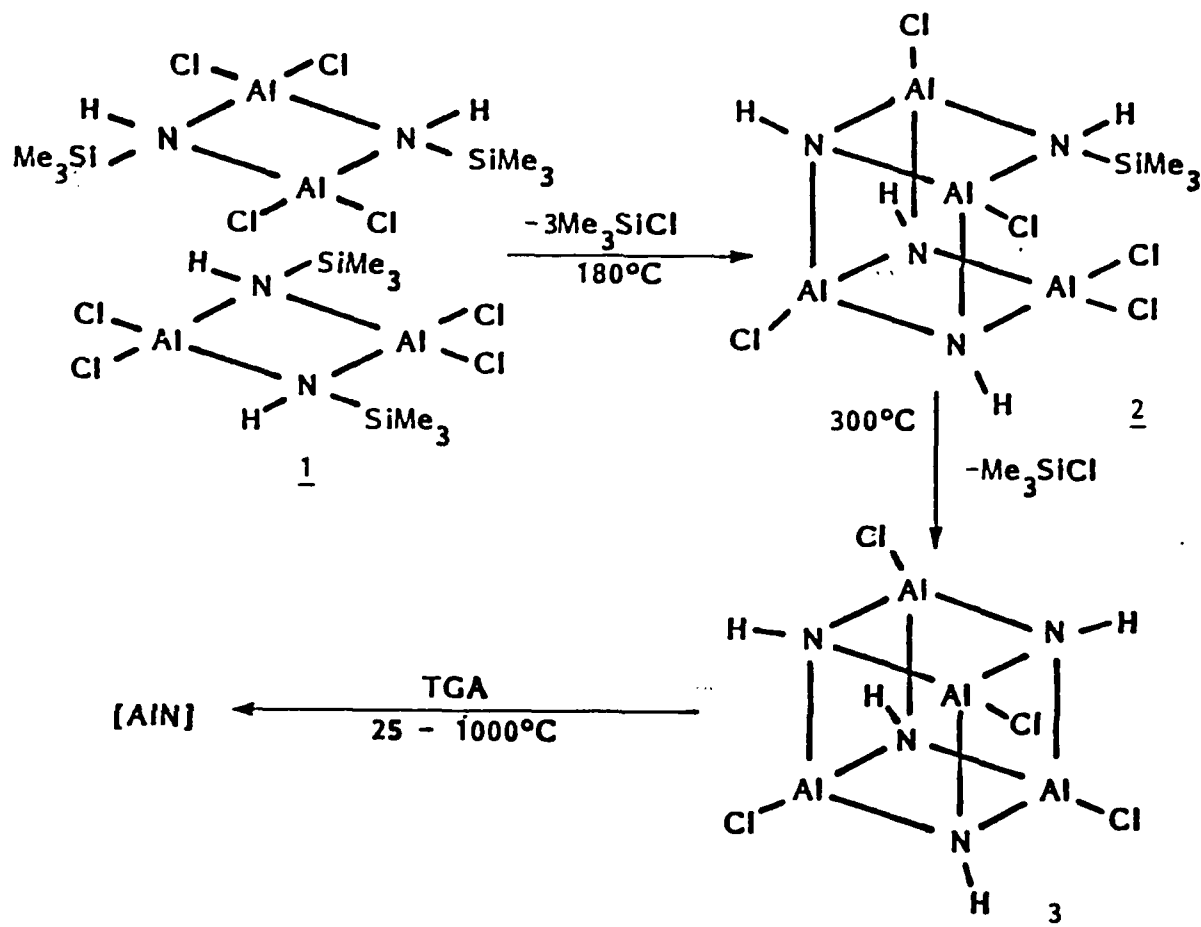
Under the conditions described by the above authors, namely conducting the interaction of hexamethyldisilazane with aluminum chloride at 40-50°C, the only product isolated was the adduct  $AlCl_3 \cdot HN(SiMe_3)_2$ , which was obtained in a 58% yield. The adduct, mp 127-130.5°C, was formed in a 89% yield when the reaction was performed in refluxing hexanes. This material was essentially quantitatively transformed into  $[AlCl_2NHSiMe_3]_2$ , mp 166-167.5°C, on heating at 138°C in an evacuated ampoule. The sealed tube process, when applied to larger quantities resulted in some adduct recovery as well as the formation of the products of further trimethylchlorosilane eliminations. It was subsequently found that prolonged reflux of the adduct in a benzene/heptane mixture, in which this material is soluble, gave a quantitative yield of  $[AlCl_2NHSiMe_3]_2$ .

Neither the melting point of the adduct nor that of the product correspond to the melting point of 272°C reported by Becke-Goehring [Ref. 12] and the 270°C published by the Russian workers [Ref. 13]. The results of later investigations by Wiberg and Schmid [Ref. 14], however, agreed with our findings. These authors prepared both  $\text{AlCl}_3 \cdot \text{HN}(\text{SiMe}_3)_2$  and  $[\text{AlCl}_2\text{NHSiMe}_3]_2$ . Their stability investigations of the adduct,  $\text{AlCl}_3 \cdot \text{HN}(\text{SiMe}_3)_2$ , revealed the material to be significantly less stable in solution than in the solid form. This explains the quantitative yield of the adduct obtained by refluxing aluminum chloride with hexamethyldisilazane in hexane (in which the adduct is insoluble), as well as its complete conversion to  $[\text{AlCl}_2\text{NHSiMe}_3]_2$  in hot benzene/heptane (in which the adduct is soluble).

Heating  $[\text{AlCl}_2\text{NHSiMe}_3]_2$  at 167-180°C resulted in evolution of trimethylchlorosilane and a residue which did not show any pronounced endotherm up to 400°C. The same product was obtained by refluxing the adduct,  $\text{AlCl}_3 \cdot \text{HN}(\text{SiMe}_3)_2$ , in hexamethyldisilazane. The presence of weak CH-absorptions (3290 and 3220  $\text{cm}^{-1}$ ) in its infrared spectrum, confirmed the retention of  $-\text{SiMe}_3$  moieties. This material was insoluble in organic solvents such as heptane, benzene, and methylene chloride. Based on the trimethylchlorosilane liberated in the pyrolysis experiment and the quantity of product obtained from  $\text{AlCl}_3 \cdot \text{HN}(\text{SiMe}_3)_2$  in hexamethyldisilazane, a structure  $[\text{AlClNH}]_3\text{AlCl}_2\text{NHSiMe}_3$  can be postulated. This was further substantiated by pyrolysis at 300°C, when the mole ratio of the trimethylchlorosilane evolved to  $[\text{AlClNH}]_3\text{AlCl}_2\text{NHSiMe}_3$  used was 1.1 to 1.0.

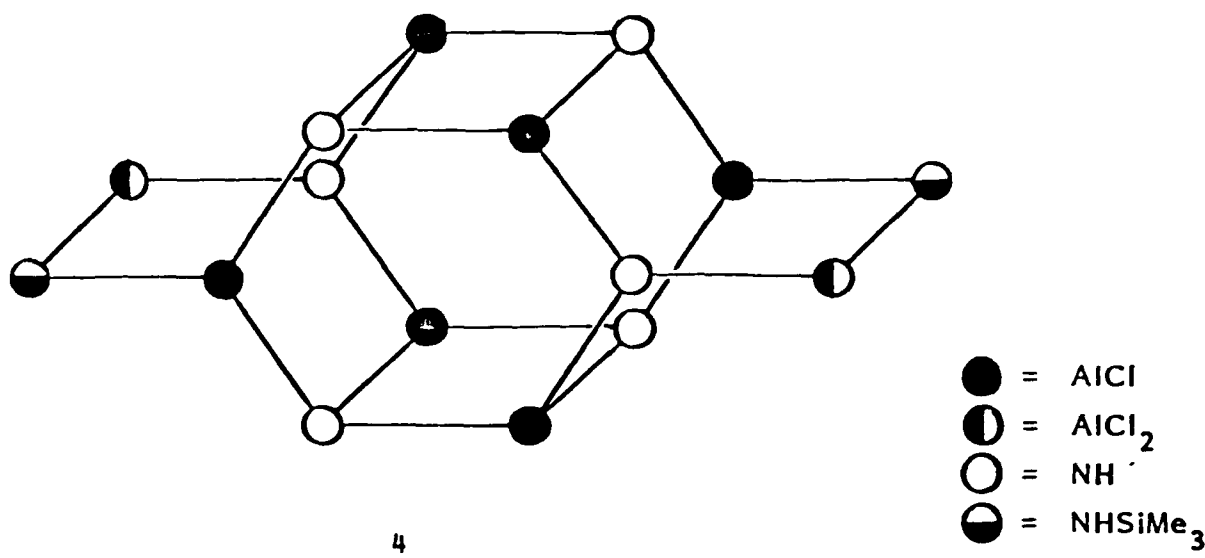
Wiberg and Schmid [Ref. 14] have established the dimer arrangement for  $[\text{AlCl}_2\text{NHSiMe}_3]_2$ . The formation of  $[\text{AlClNH}]_3\text{AlCl}_2\text{NHSiMe}_3$  from  $\text{AlCl}_3 \cdot \text{HN}(\text{SiMe}_3)_2$  proceeds most likely via compound 1 (below), since the same product was obtained from both of these materials. One can thus readily visualize the interdimer elimination of three molecules of trimethylchlorosilane leading to structure 2. Further pyrolysis then results in the symmetrical arrangement 3, i.e.,

Scheme 1



The tetramer arrangement is supported by Cesari, et al. [Ref. 15] and Cucinella, et al. [Ref. 16] (in particular based on

the dimer precursor), as well as the early work of Jones and McDonald [Ref. 17]. On the other hand hexamers were found to be more stable than tetramers [Ref. 15]. Thus, in view of the structure of  $(\text{MeAlNMe})_6(\text{Me}_2\text{AlNHMe})_2$ , having amide groups  $(\text{Me}_2\text{AlNHMe})$  bound to the imide framework, the arrangement 4 cannot be ignored [Ref. 18].

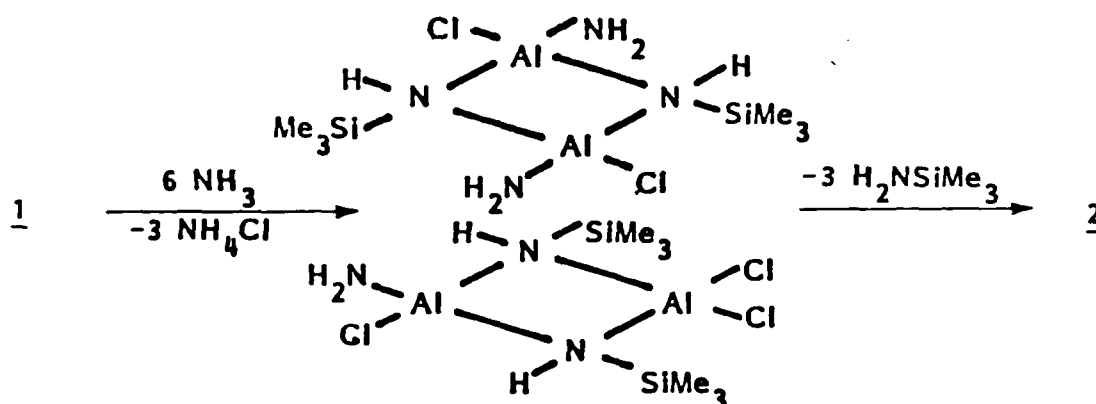


Also, Tebbe, et al. prepared what can be considered analogous compounds, e.g.,  $[\text{EtAl}^{15}\text{NH}]_{0.76}[\text{Et}_2\text{Al}^{15}\text{NH}_2]_{0.24}(\text{AlEt}_3)_{0.018}$  [Ref. 1]. However, the latter material produced both  $\text{C}_2\text{H}_6$  and  $\text{Et}_2\text{AlNH}_2$  on pyrolysis. In our case, only  $\text{Me}_3\text{SiCl}$  was evolved. Molecular weights and mass spectral data could not be obtained for 2 and 3 due to their insolubility in nonpolar solvents and infusibility. Consequently, at present the structural assignments are speculative.

The dimer  $[\text{AlCl}_2\text{NHSiMe}_3]_2$ , on treatment at room temperature with 3 moles of ammonia gave  $[\text{AlClNH}]_3\text{AlCl}_2\text{NHSiMe}_3$ .

This assignment is based on infrared spectral analysis of the insoluble product (following the removal of ammonium chloride by sublimation) and the quantity of hexamethyldisilazane formed. The quantity of ammonia consumed was somewhat higher than required for the formation of  $[\text{AlClNH}]_3\text{AlCl}_2\text{NHSiMe}_3$ ; consequently, further chlorine substitution (less than 20% of the chlorines) must have taken place. The sequence given below is proposed for the product formation in analogy with the pyrolysis process discussed in Scheme 1.

Scheme 2

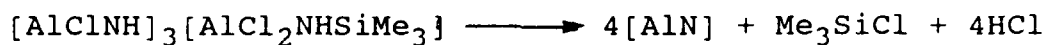


The major objective of the program was to prepare processible ceramic precursors. The dimer  $[\text{AlCl}_2\text{NHSiMe}_3]_2$  provides such a composition, as shown by the TGA data and verified by bulk pyrolysis investigations performed on the intermediate (2) and summarized in Table 1, in which aluminum nitride powders were obtained. It should be noted that to obtain aluminum nitride free from carbon requires that the process be conducted in vacuo.



TABLE 1

## BULK PYROLYSIS



Material mg	Atm	Temp <sup>a</sup> °C	Time hr	Residue		
				mg	%Theory	Color
61.8	Vac	25-965	9(3) <sup>b</sup>	15.5	64.0	Grey
138.0	N <sub>2</sub>	25-1025	9(3)	43.1	80.1	Black
203.0	Vac	25-1000	9(3)	67.3	97.6	Grey

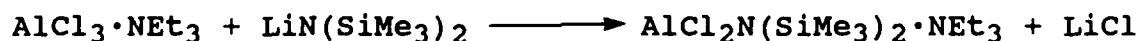
a) The temperature was increased gradually.

b) This corresponds to the time interval the sample was at the highest temperature denoted.

Using the soluble dimer  $[\text{AlCl}_2\text{NHSiMe}_3]_2$ , coatings were successfully applied to carbon composites. To prevent premature loss by sublimation during the pyrolysis, the production of the involatile and infusible intermediate 2 (or a compound wherein the chlorines were replaced by amino groups) was achieved by subjecting the coated article to ammonia treatment at room temperature. This was followed by gradual cure in vacuo to  $1000^\circ\text{C}$ . Aluminum nitride coatings on carbon were thus obtained.

### 3.2 Synthesis and Reactions of Bis(trimethylsilyl)amino-aluminum Compounds

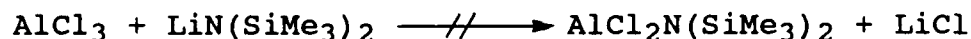
$\text{AlCl}_3 \cdot \text{NEt}_3$  was readily obtained in 97% yield using a procedure analogous to that employed in the preparation of the hexamethyldisilazane adduct. Reaction of  $\text{AlCl}_3 \cdot \text{NEt}_3$  complex with  $(\text{Me}_3\text{Si})_2\text{NH}$ , both in refluxing benzene and at  $80^\circ\text{C}$  in the absence of a solvent, gave only the unreacted starting materials. This is contrary to what has been reported for the corresponding boron complex [Ref. 24]. Treatment of  $\text{AlCl}_3 \cdot \text{HN}(\text{SiMe}_3)_2$  with triethylamine resulted in the formation of the triethylamine complex and liberation of  $(\text{Me}_3\text{Si})_2\text{NH}$ , instead of the desired dehydrohalogenation products. In view of the above, the triethylamine complex was next allowed to react with  $\text{LiN}(\text{SiMe}_3)_2$  in 1:1 molar ratio, giving  $\text{AlCl}_2\text{N}(\text{SiMe}_3)_2 \cdot \text{NEt}_3$  in a 67% yield, i.e.:



$\text{AlCl}_2\text{N}(\text{SiMe}_3)_2 \cdot \text{NEt}_3$  was characterized by elemental analysis and mass and NMR spectroscopy. The mass spectrum exhibited a  $(\text{M} - \text{CH}_3)^+$  ion at  $m/e$  343 and other ions consistent with the structure. The  $^1\text{H}$  NMR spectrum showed the methyl triplet ( $\delta$  0.82) and methylene quartet ( $\delta$  2.63) of the triethylamine and the trimethylsilyl proton resonance ( $\delta$  0.41, 0.43).

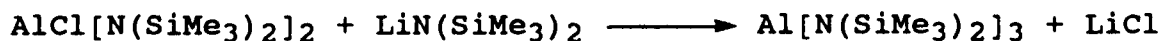
$\text{AlCl}_2\text{N}(\text{SiMe}_3)_2 \cdot \text{NEt}_3$  is extremely moisture sensitive. Exposure of an infrared sample to the atmosphere for approximately 1 min resulted in extensive hydrolysis, as shown by comparison of the infrared spectra of the unexposed and exposed materials. In the latter, bands between 2700 and 2500  $\text{cm}^{-1}$  indicated the formation of triethylamine hydrochloride.

Treatment of aluminum chloride with an equimolar amount of the lithium salt did not give the dichloro-compound, i.e.:



The only product obtained (30% yield) was  $\text{AlCl}[\text{N}(\text{SiMe}_3)_2]_2$ . The monochloro-compound was formed in a 53.9% yield employing 1:2 mole ratio of  $\text{AlCl}_3$  to the lithium salt. The mass spectrum of  $\text{AlCl}[\text{N}(\text{SiMe}_3)_2]_2$  showed a molecular ion at  $m/e$  382 as well as high intensity ions at  $m/e$  367  $[\text{M} - \text{Me}]$  and  $m/e$  347  $[\text{M} - \text{Cl}]$ .

The tri-substituted compound,  $\text{Al}[\text{N}(\text{SiMe}_3)_2]_3$ , was isolated in a 73% yield using the reaction given below:



Direct interaction of  $\text{AlCl}_3$  with the lithium salt, in a 1:3 mole ratio, afforded  $\text{Al}[\text{N}(\text{SiMe}_3)_2]_3$  in a 41% yield.

The spectroscopy data for  $\text{Al}[\text{N}(\text{SiMe}_3)_2]_3$  are consistent with the structure. The mass spectrum gave a molecular ion at  $m/e$  507 as well as a high intensity ion at  $m/e$  347 [ $\text{M} - \text{N}(\text{SiMe}_3)_2$ ]. The  $^1\text{H}$  NMR spectrum showed a single trimethylsilyl proton environment ( $\delta$  0.24).

Both the di-substituted and the tri-substituted materials were moisture sensitive, and a short exposure to atmosphere resulted in hydrolysis.  $\text{Al}[\text{N}(\text{SiMe}_3)_2]_3$  was prepared by Pump, Rochow, and Wannagat [Ref. 19] by reaction of  $(\text{Me}_3\text{Si})_2\text{NH}$  with lithium aluminum hydride. These authors reported a melting point  $>500^\circ\text{C}$ ; hydrolysis or the presence of residual salts could be responsible for the observed absence of melting.

Neither the monochloro-compound,  $\text{AlCl}[\text{N}(\text{SiMe}_3)_2]_2$ , nor the tri-substituted material,  $\text{Al}[\text{N}(\text{SiMe}_3)_2]_3$ , formed adducts with triethylamine. This finding supports the conclusions of Wiberg, Baumeister, and Zahn [Ref. 20] regarding the steric effects of bis(trimethylsilyl)amino groups on aluminum. Inasmuch as the complex  $\text{AlCl}_2\text{N}(\text{SiMe}_3)_2 \cdot \text{NEt}_3$  on reaction with an excess of  $\text{LiN}(\text{SiMe}_3)_2$  gave the tris-compound, it is obvious that the presence of triethylamine does not hinder the substitution process. Triethylamine could not be replaced in  $\text{AlCl}_2\text{N}(\text{SiMe}_3)_2 \cdot \text{NEt}_3$  by hexamethyldisilazane.

The propensity for trimethylhalosilane elimination, well documented for the boron analogues [Ref. 21,22], was also found to apply to aluminum compounds such as  $\text{AlCl}_3 \cdot \text{HN}(\text{SiMe}_3)_2$  and

$[\text{AlCl}_2\text{NHSiMe}_3]_2$ . It was anticipated that in the case of  $\text{AlCl}_2\text{N}(\text{SiMe}_3)_2 \cdot \text{NEt}_3$ , triethylamine and  $\text{Me}_3\text{SiCl}$  would be liberated, giving a cyclic derivative,  $[\text{AlClNSiMe}_3]_x$ . Exposure at  $170^\circ\text{C}$  gave approximately 15% of the expected triethylamine admixed with small quantities of trimethylsilane, tetramethylsilane, and methane. In the mass spectrum of  $\text{AlCl}_2\text{N}(\text{SiMe}_3)_2 \cdot \text{NEt}_3$ , a number of high mass fragments retained the triethylamine portion, also indicating that the complex is not readily dissociated.

Pyrolysis of  $\text{AlCl}[\text{N}(\text{SiMe}_3)_2]_2$  was investigated next. The absence of triethylamine in this material eliminated its potential interference. The product expected here was the dimer:

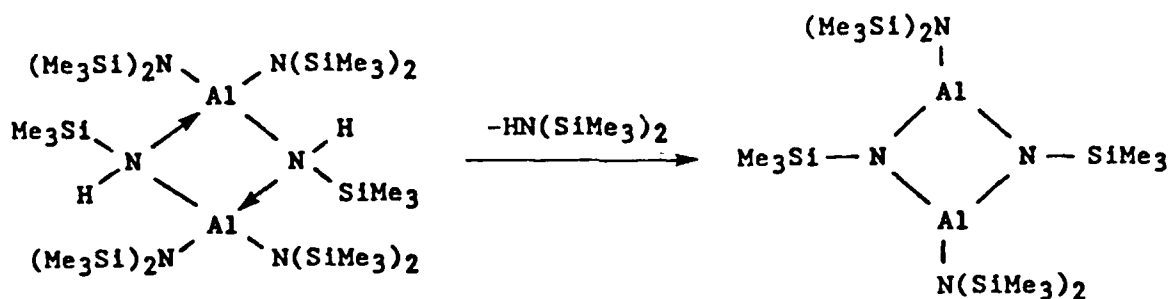


At  $150^\circ\text{C}$ , the major volatile formed was methane;  $\text{Me}_3\text{SiCl}$  amounted only to 5.6% of theory. The formation of methane points to a condensation reaction involving the methyl groups on silicon.

The symmetrical dissociation of aluminum chloride dimer upon reaction with Lewis bases under formation of neutral donor-acceptor complexes is well established [Ref. 23]. Since  $\text{AlCl}_2\text{N}(\text{SiMe}_3)_2 \cdot \text{NEt}_3$  was formed in a good yield and since in  $\text{AlCl}_3 \cdot \text{HN}(\text{SiMe}_3)_2$  the hexamethyldisilazane is readily replaced by triethylamine, it was expected that a related complex,  $\text{AlCl}_2\text{NHSiMe}_3 \cdot \text{NEt}_3$ , would result from the reaction of  $[\text{AlCl}_2\text{NHSiMe}_3]_2$  with triethylamine. The reaction consumed slightly more than one mole of triethylamine and was accompanied by the liberation of half a mole of  $(\text{Me}_3\text{Si})_2\text{NH}$  and a trace of

$\text{Me}_3\text{SiCl}$ . This finding shows that what occurs is not simply a cleavage of coordinative bridges and establishment of a coordinative bond with triethylamine. In the infrared spectrum of the product, the presence of ammonium chloride was shown by the bands at 3142, 2985, and 1412  $\text{cm}^{-1}$ ; the new absorption at 3270  $\text{cm}^{-1}$  indicated the formation of additional NH linkages. Based on these results, it can be postulated that the initial process most likely involves the evolution of  $\text{Me}_3\text{SiNH}_2$ , which decomposes into  $(\text{Me}_3\text{Si})_2\text{NH}$  and ammonia. Reaction of the ammonia produced with the chlorine substituents most likely results in the formation of the new NH moieties and ammonium chloride.

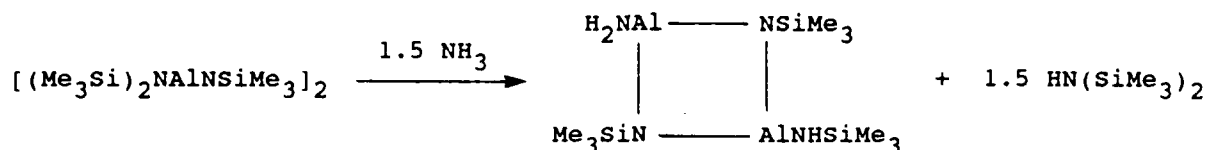
The dimer  $[\text{AlCl}_2\text{NHSiMe}_3]_2$  provides a potential starting material for the synthesis of aluminum compounds having the  $\text{NHSiMe}_3$  substituent, i.e.,  $(\text{Me}_3\text{Si})_2\text{NAl}(\text{Cl})\text{NHSiMe}_3$ ,  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{AlNHSiMe}_3$ , or  $(\text{Me}_3\text{Si})_2\text{NAl}(\text{NHSiMe}_3)_2$ . The corresponding boron analogues have been described [Ref. 24,25]. Reaction of  $[\text{AlCl}_2\text{NHSiMe}_3]_2$  with an equimolar quantity of  $\text{LiN}(\text{SiMe}_3)_2$  resulted in the recovery of some  $[\text{AlCl}_2\text{NHSiMe}_3]_2$  and a mixture of products that could be neither separated nor characterized. Employing a 1:4 ratio of  $[\text{AlCl}_2\text{NHSiMe}_3]_2$  to the lithium salt afforded a 62.7% yield of  $[(\text{Me}_3\text{Si})_2\text{NAlNSiMe}_3]_2$ . An intramolecular process, depicted below, is most likely responsible for the production of the four-membered ring compound.



The dimer arrangement is based on the measured molecular weight and the mass spectral breakdown pattern, in particular the high intensity molecular ion,  $m/e$  548. For several ions, listed below, the corresponding metastables were observed, and thus the fragmentation paths have been substantiated:  $548^+$  (M)  $\longrightarrow$   $533^+$  + Me ( $m^*$  520);  $533^+$   $\longrightarrow$   $518^+$  + Me ( $m^*$  503);  $533^+$   $\longrightarrow$   $461^+$  +  $\text{NSiMe}_2$  ( $m^*$  399);  $533^+$   $\longrightarrow$   $445^+$  +  $\text{SiMe}_4$  ( $m^*$  371). The  $^1\text{H}$  NMR spectrum showed two trimethylsilyl proton environments on the ring nitrogens ( $\delta$  0.25) and the exocyclic nitrogens ( $\delta$  0.28).

The dimer formation therefore follows the processes observed for the boron analogue which produced exclusively the four-membered ring compound [Ref. 21,26,27] rather than the trimer or tetramer. Thus, the ring size is governed by entropy (favoring the larger number of molecules, namely dimers rather than trimers or tetramers), ring strain, and substituent-caused steric factors [Ref. 28,29].

$[(\text{Me}_3\text{Si})_2\text{NAlNSiMe}_3]_2$  was found to be very moisture sensitive, shown by the appearance of absorption at  $3285\text{ cm}^{-1}$  in the IR (ascribed to NH) after a short exposure to atmosphere. Reaction with ammonia gave material for which the structure given below is proposed, i.e.,



The general arrangement is based in part on that of the starting material, on  $(\text{Me}_3\text{Si})_2\text{NH}$  evolved, ammonia consumed, elemental composition, and infrared and  $^1\text{H}$  NMR spectral data. The three bands in the N-H stretch region of the infrared spectrum in conjunction with the absorption at  $1111 \text{ cm}^{-1}$  (found to be characteristic of the  $\text{NHSiMe}_3$  group) [Ref. 30] support the presence of two types of amino hydrogens. The  $^1\text{H}$  NMR spectrum shows three different methyl proton environments with the two very close together,  $\delta$  0.40 and 0.35, being assigned to the trimethylsilyl groups on the ring nitrogens. Protons on nitrogen are known to produce broad NMR peaks at varied locations. The signals at  $\delta$  0.44 and 0.87 ppm are ascribed to the NH protons. Their relative ratio, 1:2, is in agreement with the assignments; however, the ratio of the methyl protons to the nitrogen protons, 25.7:1, is much higher than the calculated value of 9:1. This could be due to peak broadening of the NH protons. The molecular weight of 2300 indicates the compound exists in solution in a polymeric form. Difficulty was experienced in solvent removal, and efforts to obtain crystals for X-ray structure determination were unsuccessful. The material exhibited only a single endotherm in its DSC at  $\sim 275^\circ\text{C}$ . No endotherm was observed within the melting range. Thermolysis at  $280^\circ\text{C}$  gave  $(\text{Me}_3\text{Si})_2\text{NH}$  and ammonia; the ratio of the starting material to  $\text{HN}(\text{SiMe}_3)_2$  to  $\text{NH}_3$



was found to be 1:0.6:0.1. From the above ratios, the large decrease in the infrared  $1110\text{ cm}^{-1}$  absorption, and the retention of the doublet at  $3380$  and  $3290\text{ cm}^{-1}$ , one is tempted to speculate that condensation took place via the  $\text{NHSiMe}_3$  substituents.

Pyrolysis up to  $1000^\circ\text{C}$  of the low temperature thermolysis product, using TGA, resulted in a black, shiny residue pointing to carbon retention in agreement with the high ceramic yield. Conducting the final pyrolysis in a tube furnace, under an ammonia atmosphere, at  $280\text{--}990^\circ\text{C}$  gave 37.7% ceramic yield, which is higher than the 24.65% calculated for pure  $\text{AlN}$  production.

### 3.3 Reactions of Tris[bis(trimethylsilyl)amino]aluminum with Ammonia and Pyrolysis Studies

It is well established that reactions of trialkyl alanes with ammonia lead to adducts and amino- and imino-substituted alanes [Ref. 29,31]. Whether the amino-compounds are formed via the adducts [Ref. 29] or by a competing process is arguable [Ref. 32]. More recently ammonolysis was utilized in the preparation of aluminum nitride precursors [Ref. 1,4] and work is proceeding at present to further tailor this type of reaction by the use of specific substituents on aluminum and by controlling the ammonia reaction [Ref. 5-7]. In a related approach in our studies, we have utilized the reaction of ammonia with  $\text{Al}[\text{N}(\text{SiMe}_3)_2]_3$  to prepare what was visualized to be a processible precursor to pure aluminum nitride.

### 3.3.1 Starting Material Synthesis and Characterization

Reaction of  $\text{Al}[\text{N}(\text{SiMe}_3)_2]_3$  with ammonia in a 1:1 ratio gave the dimer  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{AlNH}_2$  (5). The reaction proceeded only very slowly at  $0^\circ\text{C}$  (~8% of the expected hexamethyldisilazane obtained in 4 h). There were no indications of an initial complex formation nor did  $\text{Al}[\text{N}(\text{SiMe}_3)_2]_3$  form an ether complex produced by  $\text{Al}(\text{SiMe}_3)_3$  [Ref. 23]. Conducting the reaction in ether failed to increase the dimer yield above that obtained in heptane. 5 was found to be indefinitely stable in air, in contrast to the starting material,  $\text{Al}[\text{N}(\text{SiMe}_3)_2]_3$  and  $[(\text{Me}_3\text{Si})_2\text{AlNH}_2]_2$  [Ref. 6]. It was characterized by molecular weight, mass, infrared, and NMR spectroscopy; the elemental analysis results were very poor. We have found this to be generally the case with this type of compound. The mass spectrum exhibited the molecular ion at  $m/e$  726 and a number of prominent ions derived from it, supporting further the dimer arrangement. No metastables were observed. Consequently, the actual fragmentation paths could not be established. The MS data and the molecular weight, determined by osmometry, show that  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{AlNH}_2$  exists as a dimer in the gaseous state and in solution. The presence in the infrared spectrum of two sets of doublets 3415, 3396 and 3357, 3335  $\text{cm}^{-1}$  in the  $\nu_{\text{NH}}$  region together with an absence of absorption at 1120-1165  $\text{cm}^{-1}$  eliminates the presence of  $\text{HNSiMe}_3$  groups [Ref. 30]. In the  $^1\text{H}$  NMR spectrum, two sharp, single resonances at  $\delta$  0.47 and 1.75 in the area ratio of 16.5:1 were observed in reasonable agreement with the calculated value of  $\text{CH}_3$  to  $\text{H}_2\text{N}$  protons of 18:1. The structure of 5, as

illustrated in Figure 1, confirms the dimer arrangement in agreement with the molecular weight measurements and mass spectral data. The planar four-membered,  $\text{Al}_2\text{N}_2$ , ring is approximately square, as is evident from the bond lengths  $\text{Al}(1)-\text{N}(1) = 1.944 (5) \text{ \AA}$ ,  $\text{Al}(1)-\text{N}(2) = 1.926 (5) \text{ \AA}$ , and angles  $\text{N}(1)-\text{Al}(1)-\text{N}(2) = 84.2 (2)^\circ$ ,  $\text{Al}(1)-\text{N}(1)-\text{Al}(2) = 95.3 (2)^\circ$  (see Table 2). The planar dimeric structure is analogous to that of  $[(\text{Me}_3\text{Si})_2\text{AlNH}_2]_2$  [Ref. 6] and similar to  $[\text{Me}_2\text{AlNMe}_2]_2$  [Ref. 34,35] although the endocyclic Al-N bond lengths are shorter in 5 than the average ( $1.954 \text{ \AA}$  [Ref. 6],  $1.958 \text{ \AA}$  [Ref. 34,35]) and are actually closer to those reported for six-membered  $[\text{Me}_2\text{AlNH}_2]_3$  [Ref. 5], which were found to range between  $1.921$  and  $1.942 \text{ \AA}$ .

The exocyclic Al-N bond distances, which ranged from  $1.836 (4)$  to  $1.852 (4) \text{ \AA}$ , are somewhat longer than those reported for other dimeric organoaluminum amides [Ref. 36] ( $1.798$  to  $1.827 \text{ \AA}$ ), most likely due to the bulky  $\text{SiMe}_3$  groups. The  $1.741 \text{ \AA}$  N-Si and the  $1.868 \text{ \AA}$  Si-C distances are directly comparable to those found in the trimethylsilylamino-substituted boron compounds ( $1.736$  and  $1.854 \text{ \AA}$ , respectively) [Ref. 30] and are in agreement with the  $1.874 \text{ \AA}$  Si-C average value reported for  $[(\text{Me}_3\text{Si})_2\text{AlNH}_2]_2$  [Ref. 6]. As expected for the ring system, the external  $\text{N}(5)-\text{Al}(1)-\text{N}(6)$  angle in 5 of  $120.0 (2)^\circ$  is significantly greater than the internal angles. The  $\text{Al}(1)-\text{Al}(2)$  separation in 5,  $2.870 \text{ \AA}$ , is slightly longer than in  $[(\text{Me}_3\text{Si})_2\text{AlNH}_2]_2$ , in agreement with a smaller internal angle in 5, caused by the bulky  $(\text{Me}_3\text{Si})_2\text{N}$  groups.

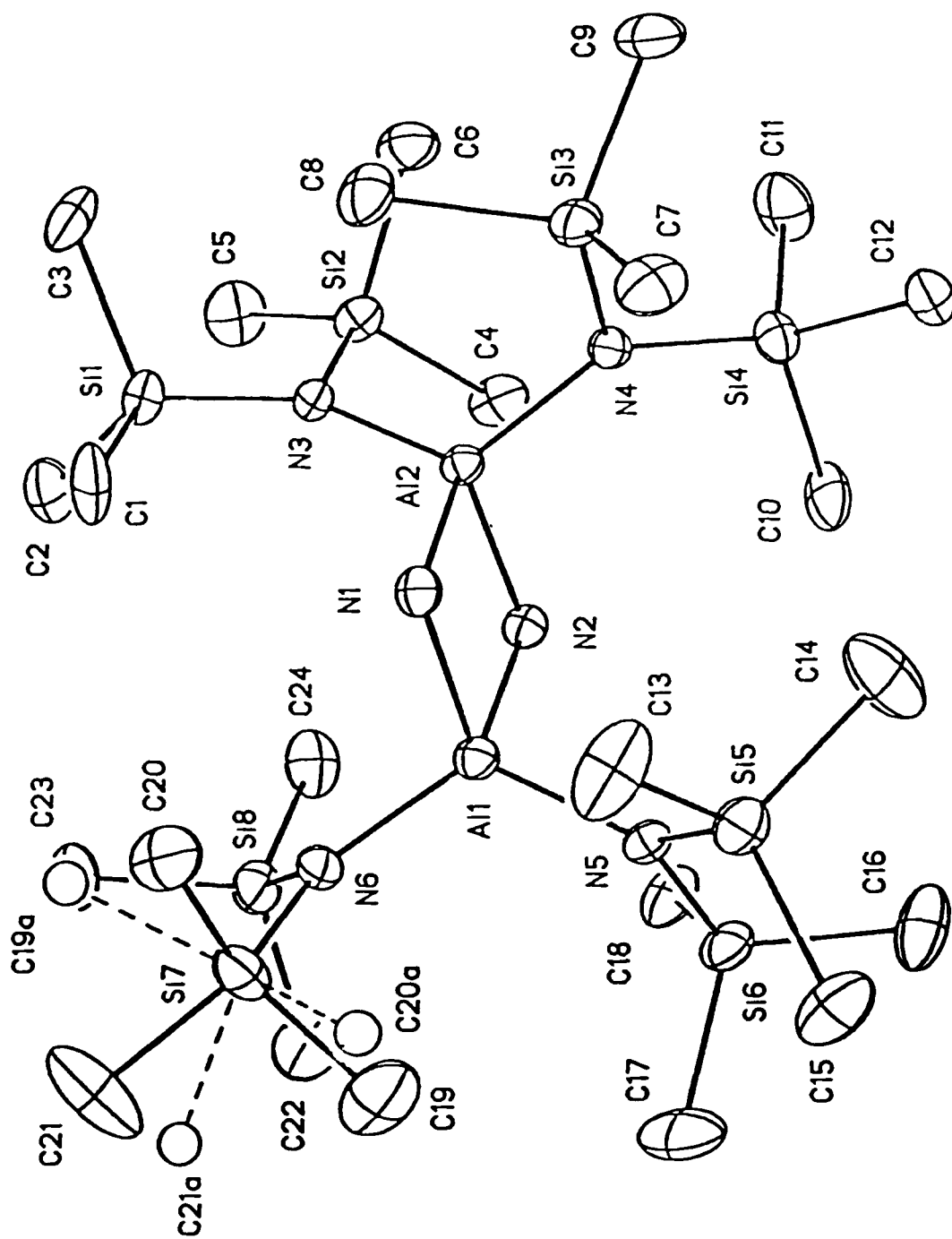
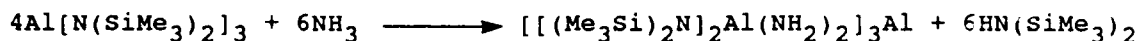


Figure 1: Thermal ellipsoid (probability level 20%) plot of  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{AlNH}_2]_2$ , the  $(\text{CH}_3)_3$  group at Si(7) is disordered. Dotted bonds and circles represent the lower (45%) of the two occupancies. Hydrogen atoms omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for  
 $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{AlNH}_2)_2$

<u>Bond Distances</u>			
Al(1)-N(1)	1.944 (5)	Si(5)-N(5)	1.735 (4)
Al(1)-N(2)	1.926 (5)	Si(6)-N(5)	1.746 (4)
Al(2)-N(1)	1.940 (5)	Si(5)-C(13)	1.864 (7)
Al(2)-N(2)	1.930 (5)	Si(5)-C(14)	1.843 (6)
Al(1)-N(6)	1.846 (4)	Si(5)-C(15)	1.863 (7)
Al(1)-N(5)	1.836 (4)	Al(1)-Al(2)	2.870 (2)
<u>Bond Angles</u>			
Al(1)-N(1)-Al(2)	95.3 (2)	Si(1)-N(3)-Si(2)	116.6 (2)
Al(1)-N(2)-Al(2)	96.2 (2)	Si(5)-N(5)-Si(6)	116.4 (2)
N(1)-Al(1)-N(2)	84.2 (2)	N(6)-Si(7)-C(19)	111.2 (8)
N(1)-Al(2)-N(2)	84.2 (2)	C(20)-Si(7)-C(21)	103.1 (13)
Al(1)-Al(2)-N(1)	42.4 (2)	N(6)-Si(7)-C(19A)	108.7 (11)
N(1)-Al(1)-N(5)	113.1 (2)	C(20A)-Si(7)-C(21A)	104.9 (17)
N(5)-Al(1)-N(6)	120.0 (2)	Si(7)-C(19A)-C(20)	70.4 (18)
Al(1)-N(6)-Si(7)	117.2 (2)	Si(7)-C(20)-C(19A)	69.2 (15)
Al(1)-N(6)-Si(8)	126.2 (2)	Si(7)-C(21A)-C(21)	69.2 (22)

Reaction of  $\text{Al}[\text{N}(\text{SiMe}_3)_2]_3$  with 2 moles of ammonia gave  $[[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\text{NH}_2)_2]_3\text{Al}$  (6), a colorless, crystalline, air-stable compound, characterized by elemental analysis, molecular weight,  $^1\text{H}$  NMR, infrared spectroscopy, and single crystal X-ray diffraction analysis. The overall process is summarized by



The mechanism of this reaction is unknown, but it has been established that 5 is not an intermediate in the formation of 6 since reaction of 5 with ammonia at room temperature resulted in a quantitative starting material recovery.

The structure of 6 given in Figure 2 is analogous to that of  $[(\text{Me}_3\text{Si})_2\text{Al}(\text{NH}_2)_2]_3\text{Al}$  [Ref. 7]. 6 crystallizes as clear prisms in monoclinic space group  $\text{C2/c}$ . It has approximate non-crystallographic  $\text{C}_3$  symmetry about the axis through the central Al atom, which is normal to the Al atoms plane (maximum deviation from a least-squares plane is 0.003 Å). All of the  $\text{Al}_2\text{N}_2$  rings are planar with a maximum deviation from the plane of 0.004 to 0.006 Å. Average Al-N( $\text{H}_2$ ) distances are 2.021 (5) Å for the central aluminum atom and 1.909 (7) Å for the remaining Al-N( $\text{H}_2$ ) distances (see Table 3). The corresponding average distances in  $[(\text{Me}_3\text{Si})_2\text{Al}(\text{NH}_2)_2]_3\text{Al}$  are 2.020 (3) and 1.931 (7) Å [Ref. 7]. The long average 2.02 Å central Al(1)-N bond in 6, while longer than the typical Al-( $\text{NH}_2$ ) bond, is comparable to values for Al-N bonds with greater than tetracoordinated Al. Examples are Al-N = 2.03 (1) Å in  $[\text{AlCl}_2(\text{bpy})_2]\text{Cl} \cdot \text{CH}_3\text{CN}$  [Ref. 37] and Al-N = 1.96 to 2.02 Å in  $\text{Al}(\text{Pc})\text{Cl}$  [Ref. 38]. The internal N-Al-N angles

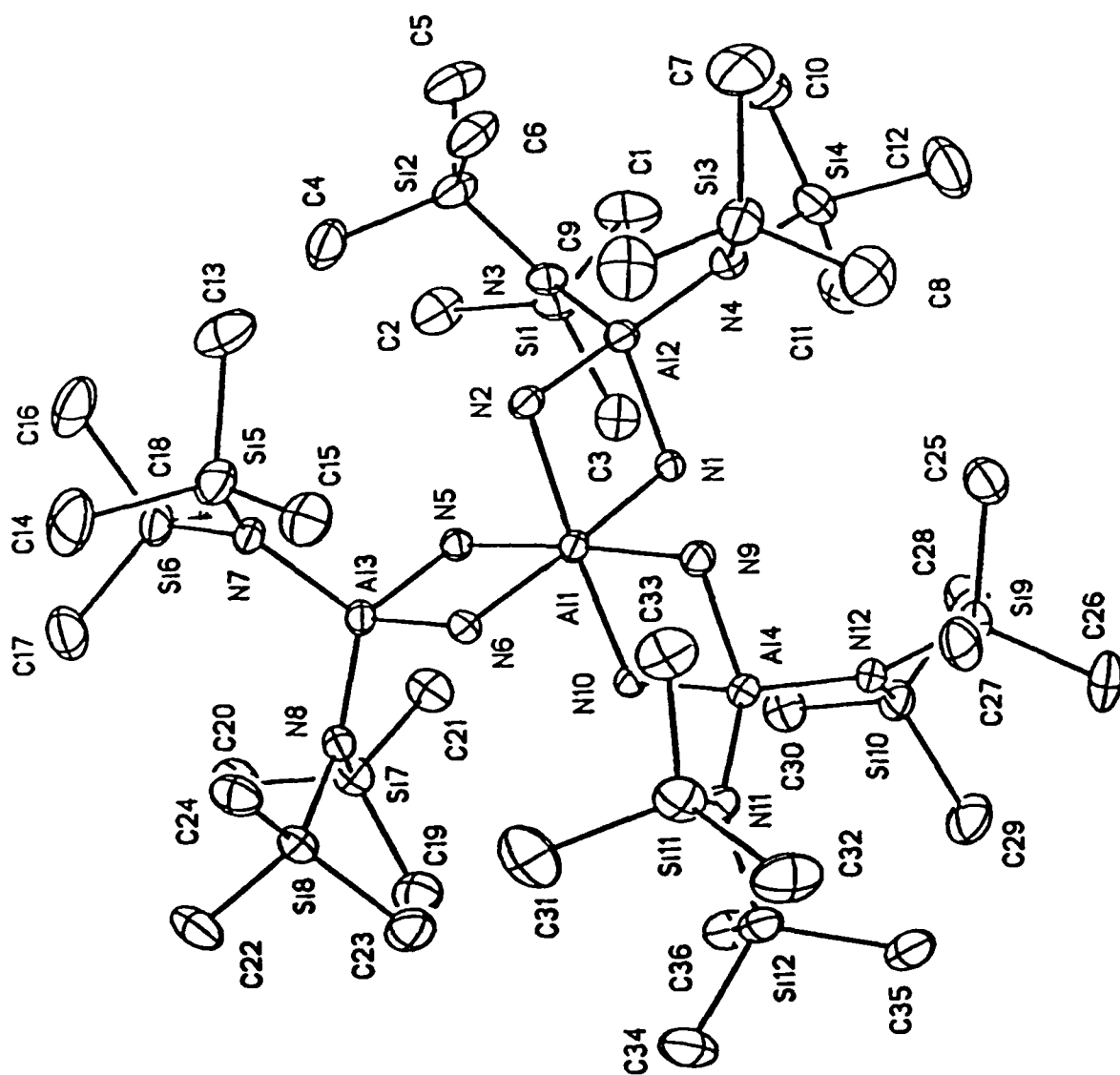


Figure 2: Thermal ellipsoid (probability level 20%) plot of  $[[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}_2(\text{NH}_2)_2]_3\text{Al}$ . Hydrogen and solvent omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) for  
 $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\text{NH}_2)_2]_3\text{Al}$

<u>Bond Distances</u>			
Al(1)-N(2)	2.024 (6)	Al(1)-N(1)	2.018 (5)
Al(1)-N(5)	2.017 (5)	Al(2)-N(2)	1.901 (6)
Al(2)-N(1)	1.912 (6)	Al(1)-Al(3)	2.897 (3)
Al(1)-Al(2)	2.903 (3)	Al(3)-N(8)	1.854 (6)
Al(2)-N(3)	1.839 (6)	N(3)-Si(1)	1.747 (6)
Al(3)-N(7)	1.852 (7)	N(4)-Si(3)	1.732 (6)
<u>Bond Angles</u>			
N(2)-Al(1)-N(6)	96.3 (2)	N(5)-Al(1)-N(10)	94.7 (2)
N(2)-Al(1)-N(5)	88.2 (2)	N(6)-Al(1)-N(10)	87.1 (2)
N(5)-Al(1)-N(6)	82.0 (2)	Al(1)-N(6)-Al(3)	95.0 (2)
N(1)-Al(1)-N(2)	81.7 (2)	N(5)-Al(3)-N(6)	88.1 (2)
Al(1)-N(1)-Al(2)	95.2 (3)	N(2)-Al(2)-N(3)	109.9 (3)
Al(1)-N(5)-Al(3)	94.9 (2)	N(3)-Al(2)-N(4)	120.6 (3)
N(1)-Al(2)-N(2)	87.8 (3)	N(1)-Al(2)-N(4)	111.1 (3)
N(1)-Al(1)-N(6)	176.3 (2)	Si(1)-N(3)-Si(2)	114.5 (3)
N(5)-Al(1)-N(9)	176.0 (2)	Si(3)-N(4)-Si(4)	115.5 (3)
N(1)-Al(1)-N(5)	94.8 (2)		



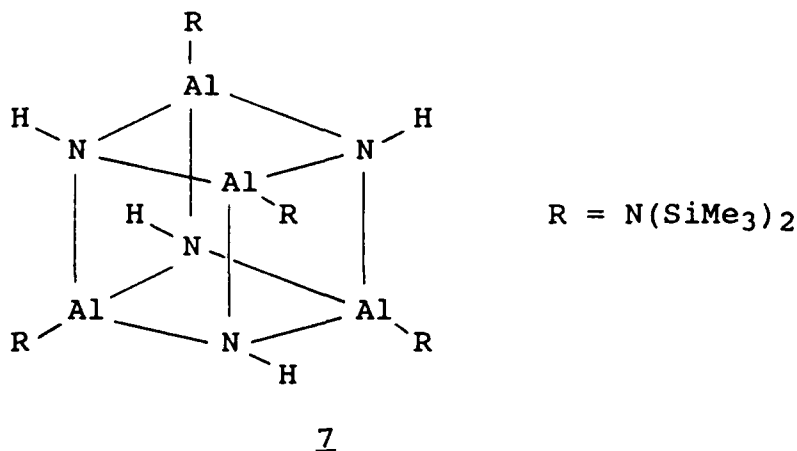
average  $82.0 (4)^\circ$  at the hexacoordinated central Al and  $88.0 (2)^\circ$  at the tetracoordinated Al atoms. Similar values of  $82.9 (2)^\circ$  and  $87.7 (2)^\circ$  were found for the  $\text{SiMe}_3$  substituted compound. For the  $(\text{Me}_3\text{Si})_2\text{N}$  substituents, the atoms are nearly planar with the maximum deviations from the Al-N-Si(-Si) planes ranging from  $0.003 \text{ \AA}$  to  $0.08 \text{ \AA}$ . Average bond distances are as follows: Al-N =  $1.850 (6) \text{ \AA}$ , N-Si =  $1.742 (7) \text{ \AA}$ , C-Si =  $1.87 (1) \text{ \AA}$ . The Al-N and N-Si distances are shortened due to N-Al and N-Si  $\pi$  bonding. Near intermolecular contacts are H--H contacts at van der Waals separation of  $2.37 \text{ \AA}$ .

The structure is consistent with infrared,  $^1\text{H}$  NMR spectroscopy, and molecular weight data. The infrared absorptions at  $3410$  and  $3330 \text{ cm}^{-1}$  agree with the presence of the  $\text{NH}_2$  bridging groups. The  $^1\text{H}$  NMR shows two different nitrogen proton environments at  $1.50$ ,  $1.44 \text{ ppm}$  and  $0.82$ ,  $0.76 \text{ ppm}$ . This could be possibly due to the amino nitrogens being diastereomeric centers. The  $8:1$  ratio of the methyl protons to the nitrogen protons, although somewhat lower than the calculated value of  $9$ , further confirms the arrangement.

### 3.3.2 Thermolysis Studies

Thermal transformation of the ammonolysis products into a higher molecular weight processible, i.e., either organic solvent soluble or fusible composition, was one of the objectives of this undertaking. The DSC of 5 exhibited a strong endotherm at  $220^\circ\text{C}$  corresponding to the melting point; no other endotherms or exotherms were observed up to  $450^\circ\text{C}$ . A DSC rerun on a sample

previously heated to 225°C did not show the 220°C endotherm, indicating decomposition. Pyrolysis of  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{AlNH}_2$  at 225°C resulted in liberation of 2 moles of hexamethyldisilazane per mole of 5. The product failed to melt up to 220°C, and no endotherm was present in its DSC up to 400°C. Based on the nature of the starting material, in conjunction with the tendency of the aluminum compounds to form eight-membered arrangements [Ref. 17] and supported by the molecular weight data and  $^1\text{H}$  NMR, it is believed that structure 7 is present here. The elemental analyses data are very poor; this was also the case with the precursor, 5. The elemental composition of 7 is based solely on the production of  $\text{HN}(\text{SiMe}_3)_2$ , which corresponds exactly to the weight loss. The reaction was repeated several times and found to be fully reproducible.



Attempts to transform  $[(\text{Me}_3\text{Si})_2\text{NAlNH}]_4$  to pure aluminum nitride were unsuccessful. Pyrolysis to 900°C in vacuo gave only 10% of the expected hexamethyldisilazane. The production of methane (mole ratio of 7 to  $\text{CH}_4$  = 1:7) indicates that silicon is retained in the residue, but it has not been determined if the

silicon is in the form of silicon nitride and/or silicon carbide. The presence of aluminum nitride in the residue was shown by an infrared absorption at  $720\text{ cm}^{-1}$  in agreement with data reported for AlN [Ref. 39]. Conducting the pyrolysis in an ammonia atmosphere, which was found to be effective in avoiding both carbon and silicon retention in the related boron compositions, was also unsuccessful. A ceramic yield of 20.23% would be expected for pure AlN; the observed ceramic yield of 58% indicates the presence of other materials in addition to AlN. Apparently  $[(\text{Me}_3\text{Si})_2\text{NAlNH}]_4$  is not amenable to further reaction with ammonia.

The DSC of  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\text{NH}_2)_2]_3\text{Al}$  exhibited an endotherm at  $196^\circ\text{C}$  corresponding to the melting point of  $191^\circ\text{C}$ . A rerun of the sample previously heated to  $250^\circ\text{C}$  failed to show the endotherm, indicating that in the vicinity of  $\sim 195^\circ\text{C}$ , decomposition occurred. 6 was thus subjected to pyrolysis in vacuo and ammonia at  $200^\circ\text{C}$ . The results of these tests are summarized in Table 4. Inasmuch as ammonia was recovered and the quantity of hexamethyldisilazane formed was the same in both experiments, indicates that at this temperature ammonia has no effect on the decomposition process. The molar ratio of hexamethyldisilazane liberated to 6 was found to be 5:1. Due to the material's insolubility in common organic solvents, structure determinations could not be made. However, it would appear, from the reproducibility of the process, that a specific arrangement is formed during the low temperature thermolysis. Further pyrolysis under TGA conditions gave a white residue, which

TABLE 4

PYROLYSES OF  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\text{NH}_2)_2]_3\text{Al}$ 

Sample		Conditions		Residue		Volatile Products			TGA Residue <sup>c</sup> %
		Temp °C	Time hr			% <sup>a</sup>	theory <sup>b</sup>	Total % <sup>a</sup>	
mg	mmol							mmol	mmol
760.7	0.652	200 <sup>d</sup>	20	27.1	14.05	72.9	3.44	none	21.7
306.6	0.263	204 <sup>e</sup>	15.5	27.0	14.05	73.0	1.36	0.54	21.8

29

- a) The percent is given with respect to the starting material employed.
- b) This value is calculated based on the arrangement  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\text{NH}_2)_2]_3\text{Al}$  and the formation of aluminum nitride.
- c) The pyrolysis residue was subjected to TGA in nitrogen; the percent of residue is calculated with respect to the original sample.
- d) Evacuated sealed ampoule was employed.
- e) The sample was sealed with 0.54 mmol of ammonia.

exhibited in its infrared spectrum a very broad, weak absorption at  $\sim 900\text{ cm}^{-1}$  and a relatively strong, broad absorption at  $730\text{ cm}^{-1}$ , characteristic for AlN [Ref. 39]. The presence of  $\text{Si}_3\text{N}_4$  and/or SiC is clearly indicated by the ceramic yield 21.8%, which is higher than the 14.06% calculated for AlN. For the composition  $6\text{AlN}\cdot\text{Si}_3\text{N}_4$ , the value is 22.0%. The pyrolysis at  $900^\circ\text{C}$  of the thermolysis intermediate in a sealed, evacuated system gave a white-gray solid. From the composition of the low temperature thermolysis product,  $\text{Al}_4\text{H}_7\text{N}_7\text{Si}_2(\text{CH}_3)_6$ , formation of  $6\text{AlN}\cdot\text{Si}_3\text{N}_4$  would require the ratio  $\text{Al}_4\text{H}_7\text{N}_7\text{Si}_2(\text{CH}_3)_6 : \text{CH}_4 : \text{NH}_3$  of 1:6:0.33. The found ratio of 1:4.7:0.52 is in relatively good agreement. The powder X-ray pattern (Figure 3a) shows the material to be partially crystalline; annealing at  $1600^\circ\text{C}$  (Figure 3b) resulted in the increased crystallization of both AlN and  $\text{Si}_3\text{N}_4$ . From the diffraction pattern, the presence of AlN and  $\beta\text{-Si}_3\text{N}_4$  admixed with a small amount ( $<5\%$ ) of  $\text{Al}_2\text{O}_3$  and a trace of  $\alpha\text{-Si}_3\text{N}_4$  is clearly evident. The formation of aluminum nitride-silicon nitride and aluminum nitride-silicon carbide ceramics having Al to Si in varying mole ratios has been reported [Ref. 40]. In the case of  $[(\text{Me}_3\text{Si})_2\text{Al}(\text{NH}_2)_2]_3\text{Al}$  [Ref. 7],  $\text{AlN}\cdot\text{SiC}$  was formed; the ratio of Al : Si was reported to be 5:1. The composition of the precursor, in our system, apparently predetermines the Al to Si ratio of 2:1, and the presence of bis(trimethylsilyl)amino instead of trimethylsilyl groups results in  $\text{Si}_3\text{N}_4$ , not SiC, production. The Al to Si ratio of 2 to 1 in the final ceramic (annealed at  $1600^\circ\text{C}$ ) was further confirmed by

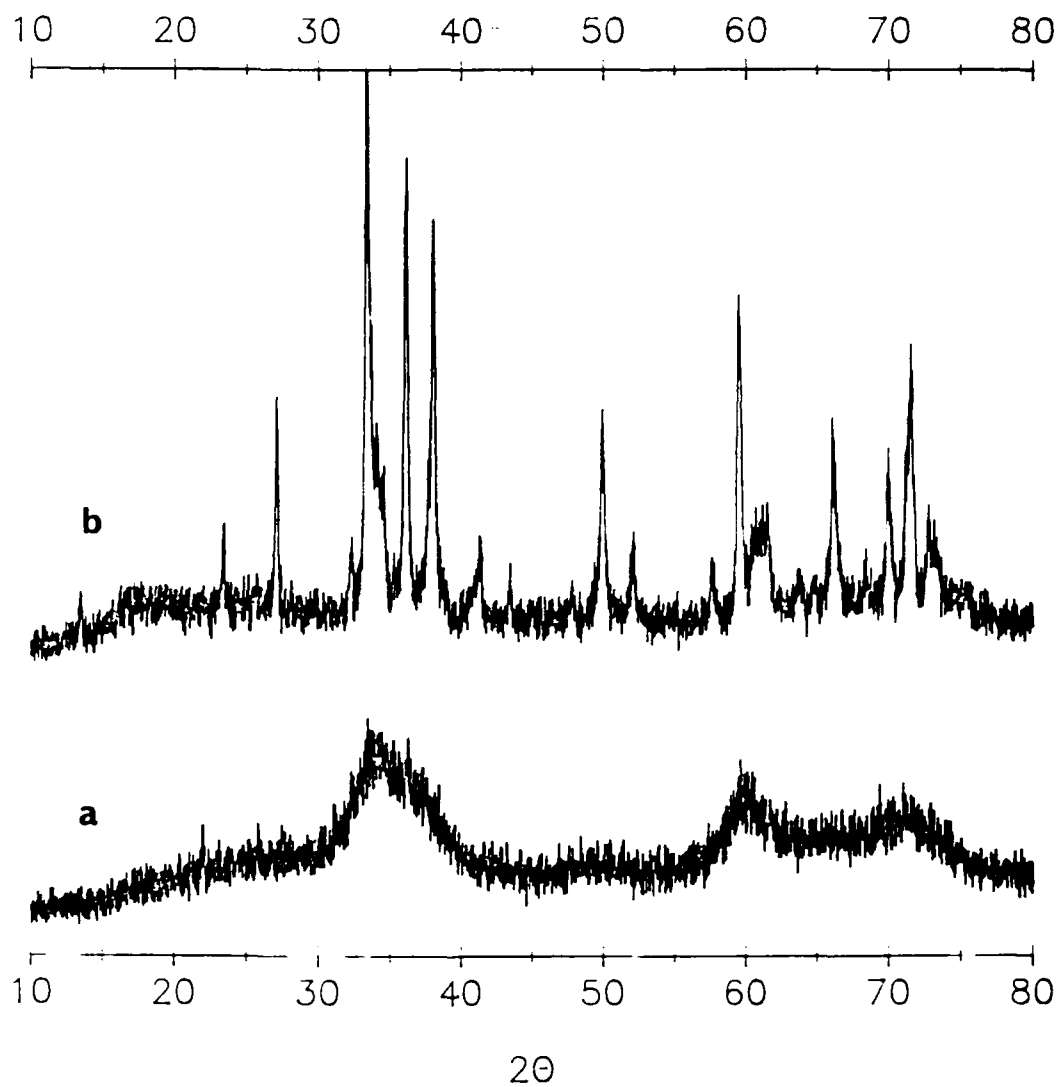


Figure 3: X-ray powder diffraction spectra from pyrolysis of  $\text{Al}_4\text{H}_7\text{N}_7\text{Si}_2(\text{CH}_3)_6$  (a) in  $\text{N}_2$  1000°C 8h/8h (b) followed by 1600°C in  $\text{N}_2$  4h/4h.

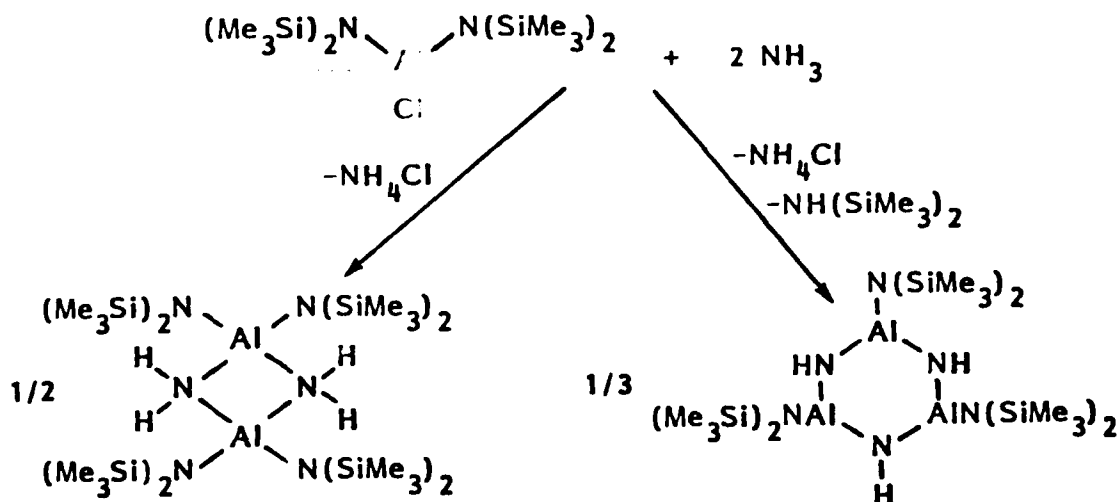
energy-dispersive X-ray analyses, which show the presence of aluminum and silicon in a 2.1:1 ratio.

When the intermediate  $\text{Al}_4\text{H}_7\text{N}_7\text{Si}_2(\text{CH}_3)_6$  was pyrolyzed in an ammonia stream at  $1000^\circ\text{C}$ , partially crystalline  $\text{AlN}$  was formed. The absence of  $\text{Si}_3\text{N}_4$  or  $\text{SiC}$  is evident from the powder X-ray pattern given in Figure 4.

Based on these investigations, the reaction of  $\text{Al}[\text{N}(\text{SiMe}_3)_2]_3$  with  $1.5 \text{ NH}_3$  resulting in 6 offers a potential precursor both to  $6\text{AlN}\cdot\text{Si}_3\text{N}_4$  and  $\text{AlN}$  ceramics. There is a definite benefit in having a ceramic composition predetermined on the molecular level since this would assure uniform properties, in particular in the case of coatings. Also multi-element ceramics would be expected to exhibit properties different from either ceramic alone.

### 3.4 Reactions of Bis[bis(trimethylsilyl)amino]aluminum Chloride with Ammonia

A reaction of the monochloro-compound,  $\text{AlCl}[\text{N}(\text{SiMe}_3)_2]_2$ , with ammonia would be expected to yield either the same product as tris[bis(trimethylsilyl)amino]aluminum or by further reaction to form either the dimer or trimer or tetramer, i.e.:



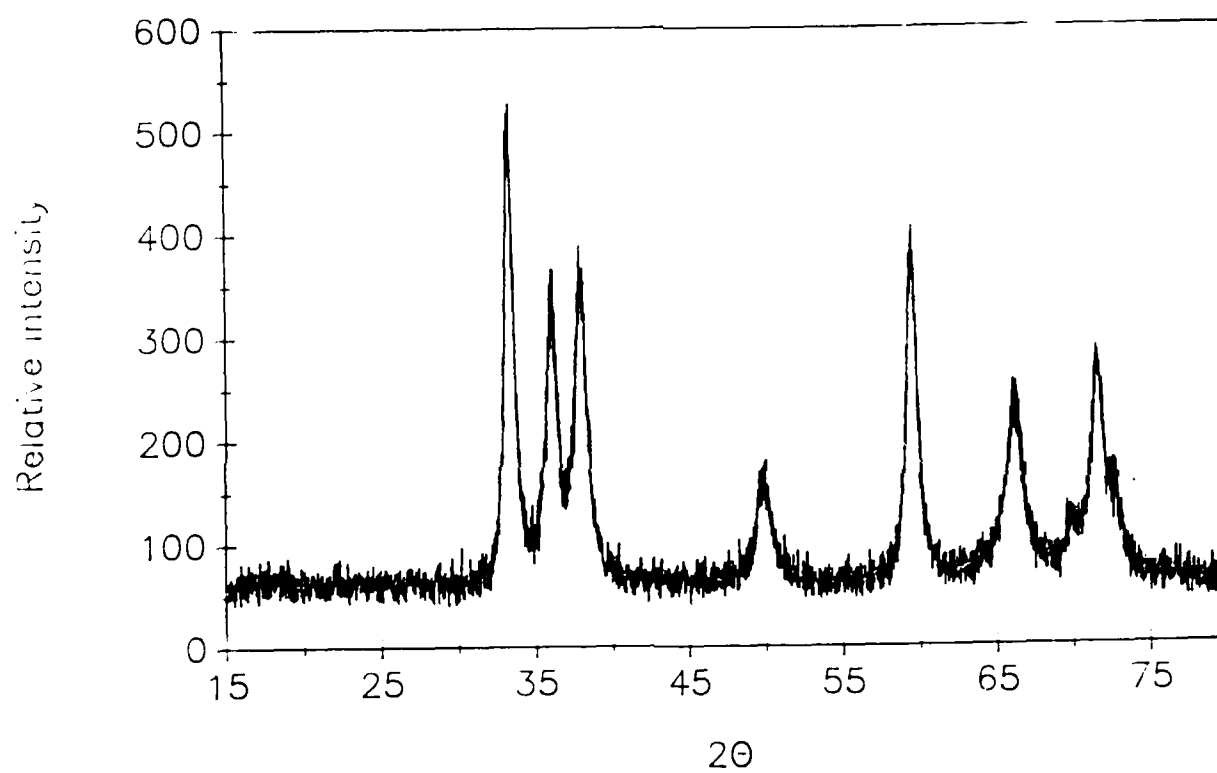


Figure 4: X-ray powder diffraction spectrum from pyrolysis of  $\text{Al}_4\text{H}_7\text{N}_7\text{Si}_2(\text{CH}_3)_6$  in  $\text{NH}_3$  1000°C 8h/8h.

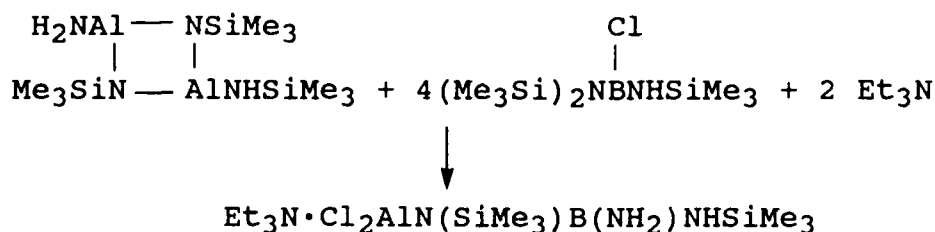


The reaction was initially conducted in a sealed ampoule kept at 0°C. From the quantity of hexamethyldisilazane evolved, a compound such as the trimer or other telomer depicted above would be expected. However, based on the mass spectral data, the product mixture does not seem to contain  $[\text{HNAI}(\text{SiMe}_3)_2]_{1-4}$ . There is some  $[\text{H}_2\text{NAI}[\text{N}(\text{SiMe}_3)_2]_2]_2$  definitely present. The crystallized portion which gave the mass spectrum consistent with the above arrangement had a melting point range of 219-221°C. The remainder of products formed, in spite of attempts at purification, could not be characterized. No crystallization took place from the spectrum of solvents tried; sublimation led to hexamethyldisilazane liberation. The material obtained on sublimation exhibited a mass spectrum essentially identical with the breakdown pattern (Table A-9) exhibited by the material (mp, 81-83°C) prepared by reacting  $\text{AlCl}[\text{N}(\text{SiMe}_3)_2]_2$  with ammonia at -20°C in hexane. The base peak and the highest m/e in this spectrum is 566<sup>+</sup>. No meaningful arrangement can be visualized for this peak as the molecular ion based on the possible groups and ions. From the poor elemental analysis and the molecular weight, infrared and mass spectral data it is impossible to deduce the composition and structure of the actual compound. Attempts to produce crystals suitable for X-ray crystal structure analysis were unsuccessful to date.

### 3.5 Multi-element or Mixed Ceramics

#### 3.5.1 AlN·BN Precursor Studies

One of the objectives of this program was to prepare precursors for AlN·BN ceramics. Mixed ceramics, in particular of well defined proportions (based on specific polymeric precursors), are of interest, since these would be expected to possess special properties. Interaction of  $\text{Me}_3\text{SiAlNHHSiMe}_3\text{NSiMe}_3\text{AlNH}_2$  with bis(trimethylsilyl)aminotrimethylsilylaminochloroborane [Ref. 24] gave an Al-N-B-N system, i.e.,



The structural arrangement is based largely on infrared spectral analysis:  $\text{Et}_3\text{N}$ ,  $3055 \text{ cm}^{-1}$ , NH,  $34220 \text{ cm}^{-1}$ ,  $\text{NHSiMe}_3$ ,  $1120\text{--}1165 \text{ cm}^{-1}$  and  $\text{AlCl}_2$ ,  $492$  and  $407 \text{ cm}^{-1}$  [Ref. 14]. The complete elemental analysis was obtained and it is in a full agreement with the proposed composition. The  $^1\text{H}$  NMR spectrum of the material purified by recrystallization from benzene shows methyl, methylene, and what is believed to be amino protons at 3.50 and 6.75 ppm in a 1:1 ratio. The location, 3.50 ppm, is in agreement with that found for  $\text{NHSiMe}_3$  (3.39 ppm) in boranes [Ref 30]. However, based on the postulated arrangement the ratio should be 1:2. Again it can be argued that the protons in the  $\text{NH}_2$  give a broad diffuse signal and thus the values found are usually low.

The ratio 7.3:1 of the methylene doublet centered at 2.3 ppm to the proton in  $\text{NHSiMe}_3$  corresponds approximately to the calculated value of 6:1. The presence of the two methyl protons resonances of equal intensity at 0.9 and 1.3 ppm agrees with the two different  $\text{SiMe}_3$  environments in the proposed structure. The other peaks can be attributed to the triplet-quartet arrangement expected from the methyl protons of the ethyl group from triethylamine. However, the ratio of methyl to methylene protons, 8.9:1, does not agree with the calculated ratio of 4.5:1, nor does the ratio 30.6:1 of methyl protons to amino protons correspond to the calculated value of 9:1. Consequently, whereas the qualitative  $^1\text{H}$  NMR data support the proposed composition the quantitative results do not. Attempts to obtain a single crystal for X-ray structure determination were not successful.

In nitrogen under the conditions of thermogravimetric analysis (TGA) from room temperature to  $1000^\circ\text{C}$  at  $10^\circ\text{C}/\text{min}$ ,  $\text{Et}_3\text{N}\cdot\text{Cl}_2\text{AlN}(\text{SiMe}_3)\text{B}(\text{NH}_2)\text{NHSiMe}_3$  gave what appeared to be pure  $\text{AlN}$  and  $\text{BN}$ . In order to confirm the production of  $\text{AlN}$  and  $\text{BN}$ , a bulk pyrolysis of the  $\text{Al-N-B-N}$  precursor was performed in a tube furnace, first under vacuum from  $25$ – $330^\circ\text{C}$ , followed by heating in an ammonia atmosphere at  $25$ – $1010^\circ\text{C}$ . A brown powdery residue was obtained. Pyrolysis of this material in nitrogen up to  $1000^\circ\text{C}$  under dynamic conditions was found by X-ray powder diffraction to contain  $\text{AlN}$  and  $\text{BN}$  (Table 5). There did not appear to be any  $\text{SiC}$  present in this material, although this could not be proven unequivocally. The presence in the infrared spectrum of broad

TABLE 5

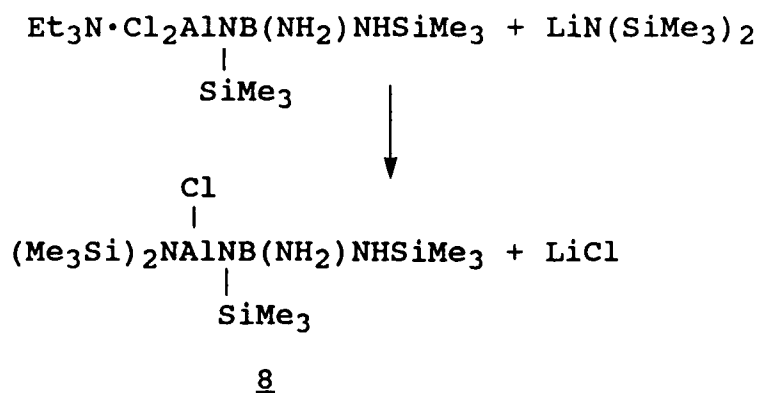
X-RAY POWDER DIFFRACTION DATA FOR  
 $\text{Et}_3\text{N} \cdot \text{Cl}_2\text{AlN}(\text{SiMe}_3)\text{B}(\text{NH}_2)\text{NHSiMe}_3$  PYROLYSIS PRODUCT  
 COMPARED TO STANDARD AlN AND BN

Pyrolysis Product (AlNBN) d-value, intensity	AlN (8-262, hex) <sup>a</sup> d-value (rel. intensity)	BN (9-12, hex) <sup>a</sup> d-value (rel. intensity)
3.3 broad, weak		3.33 (100)
2.70 strong	2.70 (100)	
Small particle size, dark background from 2.3-2.5, individual lines obscured	2.49 (60) 2.37 (70)	2.17 (16) 2.06 (6)
1.83 weak	1.83 (20)	1.82 (14) 1.67 (6)
1.52 medium	1.56 (30)	1.55 (2)
1.40 weak	1.41 (20)	1.35 (6)
1.32 weak	1.32 (18) 1.30 (8)	1.32 (4)
	1.19 (4) 1.05 (6)	1.25 (6) 1.17 (8)

a) d-values taken from JCPDS reference file, Joint Committee on Powder Diffraction Standards, Philadelphia, PA.

absorptions centered at 1380 (BN) and 725(AlN)  $\text{cm}^{-1}$  confirms the above findings. Based on the precursor's solubility in organic solvents, such as benzene, its utilization in ceramic coatings applications holds a definite promise.

To better characterize  $\text{Et}_3\text{N} \cdot \text{Cl}_2\text{AlN}(\text{SiMe}_3)\text{B}(\text{NH}_2)\text{NHSiMe}_3$ , and to resolve the  $^1\text{H}$  NMR spectral discrepancies discussed above, its reactions with the lithium salt of hexamethyldisilazane were investigated. It was expected that reaction with an equimolar amount of the lithium salt would give the monochloro-compound 8, i.e.,



However, elemental analysis of the crystals, which were isolated from this reaction, did not agree with the postulated composition as is evident from the data listed in Tables 6 and 7. Actually the values obtained, in particular the relative proportions of aluminum and boron do not make sense. The infrared spectrum is definitely changed from that of the starting material. The most significant difference is the absence of absorption at 3055  $\text{cm}^{-1}$  showing that triethylamine is no longer associated with this compound. The DSC scan of the material is also completely

TABLE 6  
ELEMENTAL ANALYSIS RESULTS

Postulated Arrangement	Empirical Formula	MW	Percent							
			C	H	Al	B	Cl	N	Si	
$\text{Et}_3\text{N} \cdot \text{Cl}_2\text{AlN}(\text{SiMe}_3)\text{B}(\text{NH}_2)\text{NHSiMe}_3$	$\text{C}_{12}\text{H}_{36}\text{AlBCl}_2\text{N}_4\text{Si}_2$	Calcd	35.91	9.04	6.72	2.69	17.67	13.96 (10.47) <sup>c</sup>	14.00	
		Found	35.82	9.45	5.49	2.71	17.80	10.7 <sup>d</sup>	15.04	
$\text{Et}_3\text{N} \cdot [\text{Cl}_2\text{AlN}(\text{SiMe}_3)\text{B}(\text{NH}_2)\text{NHSiMe}_3]_2$	$\text{C}_{24}\text{H}_{72}\text{Al}_2\text{B}_2\text{Cl}_4\text{N}_8\text{Si}_4$	Calcd	845.81	8.70	6.38	2.56	16.77	11.59	19.92	
$(\text{Me}_3\text{Si})_2\text{NAl}(\text{Cl})\text{N}(\text{SiMe}_3)\text{B}(\text{NH}_2)\text{NHSiMe}_3$	$\text{C}_{12}\text{H}_{39}\text{AlBClN}_4\text{Si}_4$	Calcd	425.06	9.25	6.35	2.54	8.34	13.18	26.43	
		Found	39.14	9.92	2.23	1.14	9.64	10.90	23.91	
$[(\text{Me}_3\text{Si})_2\text{N}]_2\text{AlN}(\text{SiMe}_3)\text{B}(\text{NH}_2)\text{NHSiMe}_3$	$\text{C}_{18}\text{H}_{57}\text{AlBN}_5\text{Si}_6$	Calcd	550.00	10.45	4.91	1.97	-	12.73	30.64	
		Found	n.d.	10.30	4.49	1.70	-	10.49	32.71	
$[(\text{Me}_3\text{Si})_2\text{N}]_2\text{AlN}(\text{SiMe}_3)\text{B}(\text{NHSiMe}_3)_2$	$\text{C}_{21}\text{H}_{65}\text{AlBN}_5\text{Si}_7$	Calcd	622.18	10.53	4.37	1.74	-	11.26	31.60	

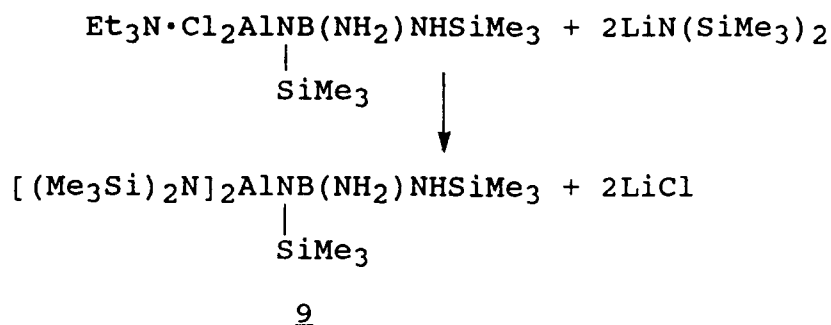
- a) The molecular weight was determined by osmometry.  
b) The molecular weight was determined by vapor pressure lowering.  
c) The value in parenthesis corresponds to the hydrolyzable nitrogen.  
d) This is the hydrolysable nitrogen analyzed as  $\text{NH}_3$ .

TABLE 7  
LISTING OF ATOM RATIOS BASED ON ELEMENTAL ANALYSIS AS COMPARED TO EMPIRICAL FORMULAS

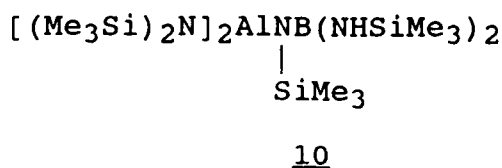
Postulated Arrangement	Empirical Formula	Found Ratios							
		C	H	Al	B	Cl	N	Si	
$\text{Et}_3\text{N} \cdot \text{Cl}_2\text{AlN}(\text{SiMe}_3)_2\text{B}(\text{NH}_2)_2\text{NHSiMe}_3$	$\text{C}_{12}\text{H}_{36}\text{AlBCl}_2\text{N}_4\text{Si}_2$	11.9	37.5	0.8	1	2	-	2.2	
$(\text{Me}_3\text{Si})_2\text{NAl}(\text{Cl})\text{N}(\text{SiMe}_3)_2\text{B}(\text{NH}_2)_2\text{NHSiMe}_3$	$\text{C}_{12}\text{H}_{39}\text{AlBClN}_4\text{Si}_4$	31	93.7	0.8	1	2.6	7.4	8.1	
$\{(\text{Me}_3\text{Si})_2\text{N}\}_2\text{AlN}(\text{SiMe}_3)_2\text{B}(\text{NH}_2)_2\text{NHSiMe}_3$	$\text{C}_{18}\text{H}_{57}\text{AlBN}_5\text{Si}_6$	20.6	65	1.1	1	-	4.8	7.4	
$\{(\text{Me}_3\text{Si})_2\text{N}\}_2\text{AlN}(\text{SiMe}_3)_2\text{B}(\text{NHSiMe}_3)_2$	$\text{C}_{21}\text{H}_{65}\text{AlBN}_5\text{Si}_7$								

different from that of the starting material. As mentioned, the elemental analysis does not agree with the expected composition; yet the residue, 15.88%, obtained under TGA conditions was close to that calculated for  $\text{AlN} \cdot \text{BN}$ , 15.48%.

Reaction of  $\text{Et}_3\text{N} \cdot \text{Cl}_2\text{AlN}(\text{SiMe}_3)\text{B}(\text{NH}_2)\text{NHSiMe}_3$  with 2 moles of the lithium salt would be expected to result in the formation of the di-substituted compound, i.e.,



The elemental analysis data as evident from the tabulations in Tables 6 and 7 agrees best with the structure as shown by:

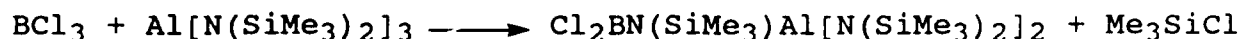


This would imply that somehow during the reaction one of the amino group hydrogens was replaced by the  $\text{SiMe}_3$  moiety. However, it is difficult to visualize such a process. The TGA results agree better with structure 9. Residue found, 11.88%; the value calculated for  $\text{AlN} \cdot \text{BN}$  based on 9, 11.96%, based on 10, 10.58%. Inasmuch as the residue was black the agreement between the



theory and the experimental result could very well be coincidental.

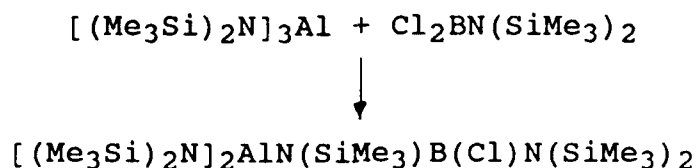
Reaction of  $\text{Al}[\text{N}(\text{SiMe}_3)_2]_3$  with  $\text{BCl}_3$ , based on literature data [Ref. 22,41,42], offered another potential route to  $\text{AlN} \cdot \text{BN}$  ceramics, i.e.:



Unreacted starting materials were recovered at  $50^\circ\text{C}$ ; at  $71^\circ\text{C}$  partial reaction took place; at  $100^\circ\text{C}$  all  $\text{BCl}_3$  was consumed and  $\text{Me}_3\text{SiCl}$ ,  $\text{Me}_4\text{Si}$ , and  $\text{Me}_3\text{B}$  were liberated. The isolation of the last two compounds shows that exchange between methyl and chloro groups occurred. Formation of  $(\text{CH}_3)_x(\text{Cl})_y\text{SiN}$  units is proposed based on the reactions of  $\text{N}(\text{SiMe}_3)_3$  and  $[(\text{Me}_3\text{Si})_2\text{NBNSiMe}_3]_2$  with boron trichloride [Ref. 43]. The ratios of  $\text{Al}[\text{N}(\text{SiMe}_3)_2]_3$  : Si liberated : B incorporated : Me liberated : Cl liberated (in  $\text{Me}_3\text{SiCl}$ ) were found to be 1:1.5:1.2:1.9:0.3. The methyl group calculation includes all the methyl groups from  $\text{Me}_3\text{B}$  and one from  $\text{Me}_4\text{Si}$ . From the above ratios, we calculate that the formation of N-B-N bridges take place to the extent of ~20%. Therefore, the resultant system contains BCl and SiCl linkages and consequently should be amenable to reactions with  $(\text{Me}_3\text{Si})_2\text{NH}$  and ammonia and lead to potential candidate precursors to ceramics containing B, N, Al, and Si.

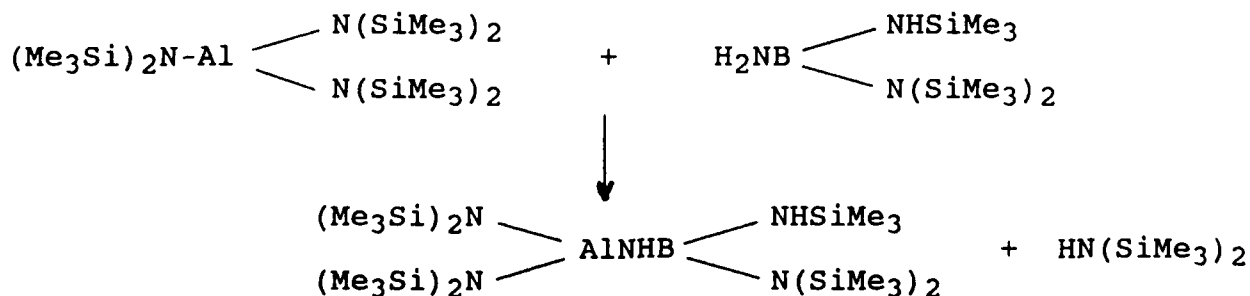
B-trichloroborazine was found to react extremely readily with hexamethyldisilazane accompanied by the evolution of trimethylchlorosilane [Ref. 44]. It was expected that the chloroborazine would also react readily with  $\text{Al}[\text{N}(\text{SiMe}_3)_2]_3$ . No

reaction took place at room temperature; however at 100°C one mole of trimethylchlorosilane per mole of the reagents was evolved. The product could not be isolated. Parallel reaction of tris[bis(trimethylsilyl)amino]aluminum with bis(trimethylsilyl)aminodichloroborane failed to result in the desired interaction namely:



or related compositions.

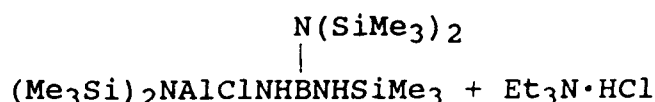
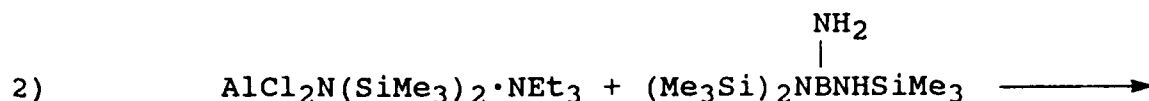
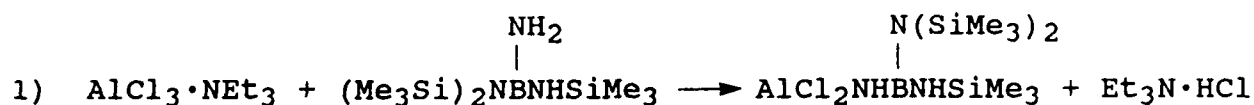
Inasmuch as tris[bis(trimethylsilyl)amino]aluminum readily undergoes stepwise aminolysis, as discussed earlier in Section 3.3, it was considered feasible that a similar replacement might occur with aminobis(trimethylsilyl)aminotrimethylsilylaminoborane, i.e.:



No reaction was observed at 100°C.

Another approach to the synthesis of AlN·BN precursors involved the interaction of two triethylamine complexes,  $\text{AlCl}_3 \cdot \text{NEt}_3$  and  $\text{AlCl}_2\text{N}(\text{SiMe}_3)_2 \cdot \text{NEt}_3$ , with aminobis(trimethylsilyl)aminotrimethylsilylaminoborane. It was visualized that

these reactions would lead to triethylamine hydrochloride elimination and establishment of an Al-N-B linkage, i.e.:



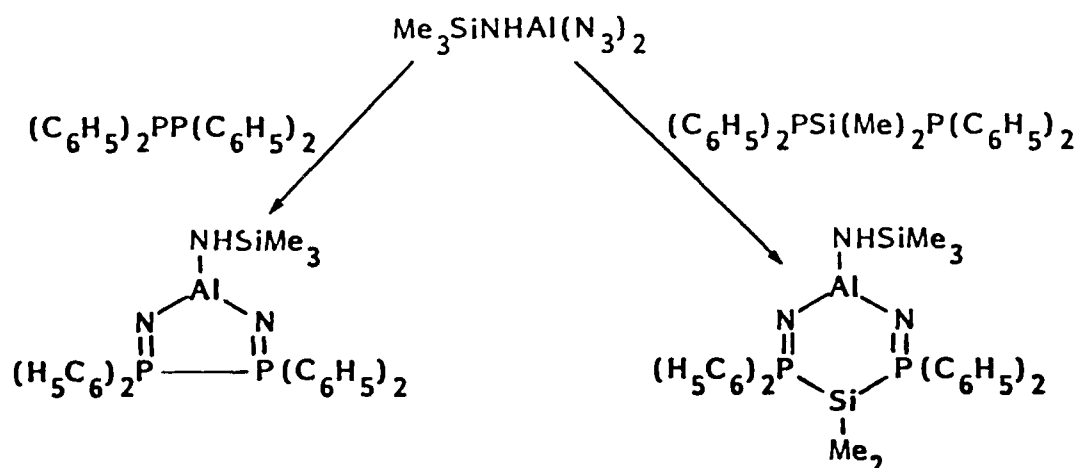
No triethylamine hydrochloride was formed in either reaction. In reaction 1 the only product isolated in 35% yield was  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{BNH}_2$ . In reaction 2  $(\text{Me}_3\text{Si})_2\text{NB}(\text{NHSiMe}_3)_2$  was found in a 50% yield; the aluminum-containing portion of the product mix was insoluble in pentane and attempts at purification were unsuccessful.

$[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\text{NH}_2)_2$  6, in view of the presence of  $\text{NH}_2$  groups, offers a potential starting material for the synthesis of compositions containing both boron and aluminum in a well-defined arrangement by utilization of chlorine-substituted boron compounds. The reactions of 6 with  $(\text{Me}_3\text{Si})_2\text{NB}(\text{Cl})\text{NHSiMe}_3$  and  $(\text{Me}_3\text{Si})_2\text{NBCl}_2$  in the presence of triethylamine at  $62^\circ\text{C}$  for 22 h, followed by further heating at  $77^\circ\text{C}$  for 16.5 h, failed to indicate any significant reaction, based on starting material recovery. On the other hand, a parallel reaction carried out using B-trichloroborazine resulted in the production of

triethylamine hydrochloride, showing that the desired dehydrohalogenation process took place to a small extent.

### 3.5.2 Al-N-P Precursor Studies

One objective of this program was to prepare ceramic precursors containing the elements P, N, Al or P, N, Si, Al. One thus could visualize an interaction of an azide such as  $\text{Me}_3\text{SiNHAL}(\text{N}_3)_2$  with tetraphenyldiphosphine or, better yet, with  $(\text{C}_6\text{H}_5)_2\text{PSi}(\text{Me}_2)\text{P}(\text{C}_6\text{H}_5)_2$ , e.g.,



To prove the feasibility of the concept, the dimer,  $[\text{AlCl}_2\text{NHSiMe}_3]_2$ , was reacted with lithium azide and triphenylphosphine in acetonitrile. The aim was to have triphenylphosphine and the azide react immediately and thus to prevent any accumulation, and therefore possible spontaneous decomposition, of the unknown diazide,  $\text{Me}_3\text{SiNHAL}(\text{N}_3)_2$ . Based on the infrared spectral evidence, the azide (either mono or diazide) was formed readily at room temperature. However, it failed to react with triphenylphosphine even in refluxing acetonitrile. In view of the above, this approach was not pursued any further.

The reaction of  $\text{BCl}_3$  with  $\text{Al}[\text{N}(\text{SiMe}_3)_2]_3$  was discussed earlier in this section. It was hoped that  $\text{PCl}_3$  would also react with the tris compound to form an Al-N-P compound. At room temperature, however, no reaction occurred.

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## 5. PUBLICATIONS AND PRESENTATIONS

### A. Presentations

A paper "Aluminum Nitride and Related Ceramics" was presented in a Poster Session at the Fourth International Conference on Ultrastructure Processing of Ceramics, Glasses, and Composites in Tucson, Arizona, February 19-24, 1989.

### B. Publications

1. "Aluminum Nitride and Related Ceramics," accepted for publication, Ultrastructure Processing of Ceramics, Glasses, and Composites, Uhlmann, D.R., Ulrich, D.R. Eds.
2. "Synthesis and Reactions of Bis(trimethylsilylamino)-aluminum Compounds," accepted for publication by Inorganic Chemistry.
3. "Reactions of Tris[bis(trimethylsilyl)amino]aluminum with Ammonia and Pyrolysis Studies," accepted for publication by Chemistry of Materials.

### C. Patents

Precursor for AlNBN Ceramic and Method of Use. Patent No. 4,946,809.

## A P P E N D I X

### Experimental Details and Procedures

## General

All solvents used were reagent grade and were dried and distilled prior to use. All the operations were carried out either in an inert atmosphere enclosure (Vacuum Atmospheres Model HE-93B), under nitrogen bypass, or in vacuo. The commercially available starting materials were usually purified by distillation, crystallization, or other appropriate means.

Infrared spectra were recorded either neat (on liquids) or as double mulls (Kel-F oil No. 10 and Nujol) using a Perkin-Elmer Corporation infrared spectrophotometer Model 1330. The mass spectrometric analyses were obtained employing a DuPont 21-491B double focusing mass spectrometer attached to a Varian Aerograph Model 2700 gas chromatograph (GC), equipped with a flame ionization detector, and a DuPont 21-094 data acquisition and processing system. Most of the mass spectra were obtained by direct insertion probe with rigid exclusion of air and moisture during loading. Gas chromatography was performed employing a 10' x 1/8" stainless steel column packed with 4% OV-101 on 80/100 mesh Chromosorb G using a programming rate of 8°C/min from 50-300°C. All thermal analyses were carried out on a DuPont 990 system with 951 TGA and DSC modules. The TGA determinations were conducted in nitrogen at 10°C/min from room temperature to 1000°C. Molecular weights were determined in benzene using a Mechrolab Model 302 vapor pressure osmometer. For moisture sensitive materials vapor pressure depression molecular weights were determined using the apparatus depicted in Figure A-1, in conjunction with a cathetometer. NMR spectra were recorded on a

Varian VXR-200 superconducting spectrometer using  $C_6D_6$  as solvent and TMS as an external standard. Vacuum line techniques were utilized where applicable; volatile products were separated by fractional condensations and quantified and identified by a combination of volume measurement, quantitative infrared spectral analysis, and GC/MS. X-ray diffraction patterns were obtained with a Philips PW 1710 automated powder diffractometer, using  $Cu K\alpha$  radiation. Energy-dispersive X-ray analyses were obtained on a JEOL JSM 840-II scanning electron microscope at 20 KeV. Both the powder diffraction and EDS X-ray analyses were performed by W. Schmidt of Rensselaer Polytechnic Institute. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. and crystal structure determinations were made by C. George, J. L. Flippen-Anderson and R. Gilardi of the Naval Research Laboratory.

#### X-ray Crystal Structure Determinations for

$[(Me_3Si)_2N]_2AlNH_2]_2$  and  $[(Me_3Si)_2N]_2Al(NH_2)_2]_3Al$

X-ray data were collected using a Nicolet R3m/V diffractometer with  $Cu K\alpha$  radiation and a highly oriented graphite crystal monochromator and were corrected for Lorentz and polarization effects. An empirical absorption correction based on the  $\phi$ -dependence of 10 reflections with  $\lambda$  ca.  $90^\circ$  was applied. Space group determinations were based on the extinctions present and the E value statistics, and were confirmed by the structure solutions. Calculations were carried out using SHELXTL. The parameters refined by full matrix least squares methods include

the atom coordinates and anisotropic thermal parameters for all nonhydrogen atoms. The function minimized during least-squares refinement was  $\sum w (F_o - F_c)^2$ . Scattering factors and corrections for anomalous dispersion were from International Tables for X-ray Crystallography. The methyl hydrogens were treated as rigid groups and allowed to rotate about the Si-C bonds with the coordinate shifts of the carbon atoms applied to the bonded hydrogens; the C-H bond length was fixed at 0.96 Å and angle H-C-H at 109.5°. Further details of data collection and refinement are given in Table A-1. Tables of complete bond lengths, bond angles, anisotropic displacement coefficients, hydrogen atom coordinates and isotropic displacement coefficients, and observed and calculated structure factors are available upon request.

A single crystal of  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{AlNH}_2]_2$ , 0.63 x 0.31 x 0.34 mm, obtained as a colorless needle from a saturated hexane solution and sealed in a thin capillary under helium, was employed. Methyl hydrogen isotropic thermal parameters were restrained to be equal within the compound for all but the  $\text{Me}_3$  group on Si(7). These methyl groups were disordered and the hydrogens were fixed at idealized positions with their own set of isotropic thermal parameters. The amino hydrogens were refined isotropically. Atomic coordinates and the equivalent isotropic displacement coefficients are given in Table A-2, pertinent bond distances and angles in Table 2.

A single crystal of  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\text{NH}_2)_2]_3\text{Al}$ , 0.22 x 0.25 x 0.37 mm, obtained as a colorless prism from a saturated hexane solution, co-crystallized with hexane in a 2:1 ratio.

Determination was made in air. Methyl hydrogen isotropic thermal parameters were restrained to be equal. The amino hydrogens were fixed at idealized positions with common isotropic thermal parameters. The hexane solvent, which sits on a center of symmetry, is poorly defined and was refined isotropically. Atomic coordinates and the equivalent isotropic displacement coefficients are given in Table A-3, pertinent bond distances and angles in Table 3.

#### Preparation of $\text{AlCl}_3 \cdot \text{HN}(\text{SiMe}_3)_2$

Under nitrogen bypass, to a stirred suspension of freshly sublimed, pure aluminum chloride (4.98 g, 37.35 mmol) in hexane (20 ml) was added hexamethyldisilazane (12.52 g, 77.57 mmol) at 50°C over a 15 min period. The reaction mixture was subsequently refluxed for an additional 3 hr. On cooling, 9.78 g (88.8% yield) of the moisture-sensitive adduct was obtained. Crystallization from heptane gave 78.5% yield of crystals, mp 127-130.5°C, Anal. Calcd for  $\text{C}_6\text{H}_{19}\text{AlCl}_3\text{NSi}_2$ : Cl, 36.09; N, 4.75. Found: Cl, 36.52; N, 5.06. DSC, Figure A-2.

#### Preparation of $[\text{AlCl}_2\text{NHSiMe}_3]_2$

##### a) From pyrolysis of $\text{AlCl}_3 \cdot \text{HN}(\text{SiMe}_3)_2$

The adduct,  $\text{AlCl}_3 \cdot \text{HN}(\text{SiMe}_3)_2$  (470.7 mg, 1.597 mmol), was sealed in vacuo and heated at 138°C for 3.75 hr; a white solid resulted. After cooling and opening to the vacuum system, trimethylchlorosilane, 162.3 mg (93.5% yield) was collected. The solid residue (250 mg, 84.2% yield) was crystallized from benzene/heptane, mp 166-167.5°C, Anal. Calcd for

$C_6H_{20}Al_2Cl_4N_2Si_2$ . Cl, 38.11; N, 7.53. Found: Cl, 38.12; N, 7.08. DSC, Figure A-3.

b) By prolonged reflux of  $AlCl_3 \cdot HN(SiMe_3)_2$  in benzene/heptane solution

The adduct,  $AlCl_3 \cdot HN(SiMe_3)_2$  (30.25 g, 102.6 mmol) was dissolved in 1:10 benzene/heptane mixture (300 ml) and the resulting solution was then refluxed for 35 hr. On cooling, the product,  $[AlCl_2NHSiMe_3]_2$ , 18.02 g (94.3% yield), mp 167.5-170°C, was obtained.

Preparation of  $[AlClNH]_3AlCl_2NHSiMe_3$

a) From the pyrolysis of  $[AlCl_2NHSiMe_3]_2$

The dimer,  $[AlCl_2NHSiMe_3]_2$ , (545.1 mg, 1.465 mmol) was heated in vacuo in a sealed tube at 167-180°C for 15.75 hr; the only volatile produced was trimethylchlorosilane (221.1 mg, theory 238.7 mg). DSC, Figure A-4.

b) By prolonged reflux of  $AlCl_3 \cdot HN(SiMe_3)_2$  in hexamethyldisilazane

A mixture of  $AlCl_3 \cdot HN(SiMe_3)_2$  (4.00 g, 13.57 mmol) and hexamethyldisilazane (26.44 g, 163.8 mmol) was heated under reflux for 3 hr. Initially, the solution cleared; subsequently, a solid started to appear. After cooling, the solid, 1.31 g, was filtered off; evaporation of solvent yielded an additional 150 mg. The product failed to melt to 200°C; it exhibited an infrared spectrum identical with that of the material obtained from  $[AlCl_2NHSiMe_3]_2$  after heating at 167-180°C. Assuming the structure  $(AlClNH)_3AlCl_2NHSiMe_3$ , the yield was quantitative.



Anal. Calcd for  $C_3H_{13}Cl_5N_4Al_4$ : Cl, 42.36; N, 13.4. Found: Cl, 38.8; N, 12.9. -Infrared spectrum, Figure A-5.

#### Preparation of $[AlClNH]_4$

$[AlClNH]_3AlCl_2NHSiMe_3$  (140.1 mg, 0.335 mmol), was pyrolyzed in an evacuated, sealed tube at 300°C for 2 hr. The condensable volatiles consisted only of trimethylchlorosilane (30.9 mg, 0.296 mmol). Infrared spectrum, Figure A-6. Thermogravimetric analysis (TGA), in nitrogen, of the product conducted at 10°C/min from room temperature to 1000°C gave 53.7% of residue; theory  $(AlClNH)_x \longrightarrow (AlN)_x$ , 52.9%. The grey powder exhibited an infrared spectrum identical with that of commercial AlN.

#### Interaction of $[Me_3SiNHAlCl_2]_2$ with ammonia

A solution of  $[Me_3SiNHAlCl_2]_2$  (542.1 mg, 1.457 mmol) in toluene (975.5 mg) was sealed in an evacuated tube with ammonia (4.522 mmol). After a 24 hr exposure at room temperature, the tube was opened and the volatiles were fractionated from a warming trap through traps cooled to -47, -78, and -196°C; 2.776 mmol of ammonia were recovered showing that 15% of the chlorines were substituted. Accordingly, all the products were recombined and exposed to 35°C for 94 hr. No ammonia was recovered. A trace of trimethylchlorosilane (0.1 mmol) was also produced. The residue, 440 mg, was composed of ammonium chloride (which was subsequently removed by sublimation at 125°C) and an involatile residue which exhibited an infrared absorption identical with that of  $[NHAlCl]_3AlCl_2NHSiMe_3$ . Based on  $[Me_3SiNHAlCl_2]_2$

employed, a 422.2 mg residue ( $\text{NH}_4\text{Cl}$ , 117.5 mg;  $[\text{NHAlCl}]_3\text{AlCl}_2\text{NHSiMe}_3$ , 304.7 mg) and 1.225 mmol ammonia recovery would be expected. Since no ammonia was recovered, further amino substitution must have taken place.

#### Coating of carbon-carbon composite

A 13 mm x 8 mm and 3 mm thick carbon-carbon composite received from GA Technologies, Inc. was washed with benzene and heated in vacuo to 980°C over a 2 hr period. Subsequently, in an inert atmosphere enclosure the thus treated composite was dipped into a solution containing 0.5 g of  $[\text{Me}_3\text{SiNHAlCl}_2]_2$  in 4 ml of benzene. The coated composite was then heated in nitrogen atmosphere, 500 mm at 150-188°C for 0.75 hr. After cooling and nitrogen removal, the material was heated in vacuo gradually over a period of 3 hr from room temperature to 970°C. The post-cure was conducted in ammonia (500 mm) again utilizing gradual heat increase from room temperature to 990°C over 7 hr. The weight gain was 2.7 mg, which based on the surface area of 334 mm<sup>2</sup> corresponded to a 5μ thick film.

#### Preparation of $\text{AlCl}_3 \cdot \text{N}(\text{C}_2\text{H}_5)_3$

Under a nitrogen bypass, to a stirred suspension of freshly sublimed, pure aluminum chloride (8.97 g, 67.27 mmol) in hexane (37 ml) was added triethylamine (13.70 g, 135.38 mmol) at 50°C over 25 min. This was followed by a 3 hr reflux. On cooling, 15.29 g (96.9% yield) of extremely moisture-sensitive product was obtained. Crystallization from benzene/heptane gave

11.34 g (71.9% yield) of the product, mp 119-122°C. Anal. Calcd for  $\text{AlC}_6\text{H}_{15}\text{Cl}_3\text{N}$ : Cl, 45.35. Found: Cl, 46.11.

Interaction of  $\text{AlCl}_3 \cdot \text{N}(\text{C}_2\text{H}_5)_3$  with hexamethyldisilazane

a) In benzene at reflux

Under nitrogen bypass, a mixture of  $\text{AlCl}_3 \cdot \text{N}(\text{C}_2\text{H}_5)_3$  (3.47 g, 14.80 mmol) and hexamethyldisilazane (4.87 g, 30.17 mmol) in benzene (25 ml) was refluxed for 4 hr. After solvent removal in vacuo, the solid obtained (3.59 g) exhibited an infrared spectrum identical to that of the starting material.

b) Neat at 80°C

Under nitrogen bypass, a mixture of  $\text{AlCl}_3 \cdot \text{N}(\text{C}_2\text{H}_5)_3$  (970 mg, 4.14 mmol) and hexamethyldisilazane (1.39 g, 8.05 mmol) was stirred at 80°C over a period of 20 hr. Two layers were present; on cooling, the bottom portion of the solution solidified. On filtration, 910 mg of solid was obtained; its infrared spectrum was identical with that of the starting material.

c) In refluxing hexamethyldisilazane

Under nitrogen bypass, a mixture of  $\text{AlCl}_3 \cdot \text{N}(\text{C}_2\text{H}_5)_3$  (990 mg, 4.22 mmol) was refluxed in hexamethyldisilazane (2.29 g, 14.19 mmol) over a period of 16 hr. On cooling, a dark, sticky solid collected at the bottom of the clear solution. The solid exhibited absorption in the 2900-2480  $\text{cm}^{-1}$  region, indicative of a salt; however, the material did not seem to contain triethylamine hydrochloride.

#### Treatment of $\text{AlCl}_3 \cdot \text{HN}(\text{SiMe}_3)_2$ with triethylamine

A mixture of  $\text{AlCl}_3 \cdot \text{HN}(\text{SiMe}_3)_2$  (1.0 g, 3.4 mmol) and triethylamine (1.72 g, 17.0 mmol) in benzene (5 mL) was refluxed for 20 hr under nitrogen bypass. No precipitate was formed; the reaction mixture was evaporated in vacuo. The volatiles consisted of benzene, triethylamine, and  $(\text{Me}_3\text{Si})_2\text{NH}$ ; the solid residue (0.80 g) consisted of  $\text{AlCl}_3 \cdot \text{NEt}_3$  complex as determined from comparison of its infrared spectrum with that of an authentic sample.

#### Reaction of $\text{AlCl}_3 \cdot \text{NEt}_3$ complex with $\text{LiN}(\text{SiMe}_3)_2$

To a stirred solution of  $\text{AlCl}_3 \cdot \text{NEt}_3$  (1.40 g, 6.0 mmol) in benzene (5 mL) was added the lithium salt (1.00 g, 6.0 mmol) in benzene (10 mL) over a period of 10 min. After standing at room temperature for 3 days, the cloudy solution was evaporated in vacuo. The residue, 2.26 g, was treated with benzene. The insoluble  $\text{LiCl}$ , 240 mg (96% yield), was filtered off. The solid, 1.99 g (92.6% yield), recovered after benzene removal, was crystallized from hexane giving 1.44 g (67.0% yield), mp  $104-106^\circ\text{C}$ , of  $\text{AlCl}_2\text{N}(\text{SiMe}_3)_2 \cdot \text{NEt}_3$ . Another recrystallization from hexane gave 0.66 g, mp  $105-106^\circ\text{C}$ . Anal. Calcd for  $\text{C}_{12}\text{H}_{33}\text{AlCl}_2\text{N}_2\text{Si}_2$ : C, 40.10; H, 9.25; Al, 7.51; Cl, 19.73; N, 7.79. Found: C, 39.60; H, 9.02; Al, 7.21; Cl, 20.2; N, 7.91. Infrared spectrum ( $\text{cm}^{-1}$ , KBr plates); 2988 (m), 2950 (m), 2900 (m), 1452 (m), 1398 (w), 1388 (w), 1253 (s), 1178 (m), 1167 (w), 1156 (m), 1082 (m), 1031 (m), 1006 (w), 900 (s, br), 865 (s, br), 841 (s, br), 766 (m), 731 (m), 713 (m), 678 (m), 667 (m), 620

(w), 490 (s), 470 (s), 395 (s). Complete infrared spectra, Figures A-7, A-8. MS (70 eV), m/e (relative intensity, ion): 343 (2.5%, M - Me), 242 (4.7%, M - Me - N $\text{Et}_3$ ), 198 (12.4%, M - N(SiMe $_3$ ) $_2$ ), 169 (14.8%, M - N(SiMe $_3$ ) $_2$  - Et), 161 (20.3%, HN(SiMe $_3$ ) $_2$ ), 146 (100%, Me $_3$ Si(Me $_2$ Si)NH). Complete mass spectrum, Table A-4.  $^1\text{H}$  NMR (C $_6$ D $_6$ ):  $\delta$  0.41, 0.43 (18H, CH $_3$ Si), 0.82 (9H, CH $_3$ ), 2.63 (6H, CH $_2$ ).

Reaction of aluminum chloride with LiN(SiMe $_3$ ) $_2$  in 1:2 mole ratio

To a stirred solution of the lithium salt (6.0 g, 35.9 mmol) in benzene (35 mL) was added aluminum chloride (2.40 g, 18.0 mmol) over a 1 hr period. Next day a fine precipitate, 2.00 g (LiCl expected, 1.58 g), was filtered off. Solvent removal from the filtrate afforded AlCl[N(SiMe $_3$ ) $_2$ ] $_2$  as a yellow liquid, 6.29 g. Distillation at 0.001 mm Hg gave: 0.26 g (bp 57-58°C); 3.45 g (bp 60-63°C); and 0.78 g (bp 67-71°C); fractions 1 and 2 (53.9% yield) exhibited identical infrared spectra; the material crystallized on standing, mp 30-31°C. Anal. Calcd for C $_{12}$ H $_{36}$ AlClN $_2$ Si $_4$ : C, 37.61; H, 9.47; Al, 7.04; Cl, 9.25; N, 7.31. Found: C, 37.10; H, 9.59; Al, 7.30; Cl, 9.41; N, 7.81. Infrared spectrum (cm $^{-1}$ , capillary film, KBr plates) 2950 (m), 2895 (w), 1441 (w, br), 1400 (w, br), 1251 (s), 1195 (w, sh), 1054 (w), 1045 (w), 922 (s, br), 895 (s, br), 860 (s), 836 (s), 757 (m), 672 (m), 613 (w), 520 (s), 373 (m). Complete infrared spectrum, Figure A-9. Mass spectrum (70 eV), m/e (relative intensity, ion): 382 (6.7%, M), 367 (44.5%, M - Me), 347 (68.5%, M - Cl),

275 (100%,  $(\text{Me}_3\text{Si})_2\text{NAlNHSiMe}_3$ ), 259 (38.7%,  $\text{M} - \text{Me} - \text{Me}_3\text{SiCl}$ ), 187 (23.2%,  $(\text{Me}_3\text{Si})_2\text{NAl}$ ). Complete mass spectrum Table A-5.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  0.23, 0.25 ( $\text{CH}_3\text{Si}$ ).

Reaction of aluminum chloride with  $\text{LiN}(\text{SiMe}_3)_2$  in 1:3 mole ratio

To a stirred solution of the lithium salt (5.0 g, 29.9 mmol) in benzene (25 mL) was added aluminum chloride (1.33 g, 9.97 mmol) over a period of 20 min. Stirring at room temperature was continued for 3 days; the precipitated  $\text{LiCl}$  (1.19 g, 93% yield) was filtered off. Removal of the solvent in vacuo afforded a solid (5.36 g); dissolution in pentane resulted in additional 40 mg of  $\text{LiCl}$ . Fractional crystallization of the pentane soluble material from Freon-113 gave 2.07 g (40.8% yield) of  $\text{Al}[\text{N}(\text{SiMe}_3)_2]_3$ , mp 215-217°C. Anal. Calcd for  $\text{C}_{18}\text{H}_{54}\text{AlN}_3\text{Si}_6$ : C, 42.55; H, 10.71; Al, 5.31; N, 8.27; MW, 508.15. Found: C, 42.05; H, 10.40; Al, 5.53; N, 8.52; MW, 470 (pentane vapor pressure depression at 16°C). Infrared spectrum ( $\text{cm}^{-1}$ , KBr plates) 2971 (s), 2955 (s), 2908 (m), 1440 (w), 1403 (w), 1291 (m), 1250 (s, br), 900 (s, br), 857 (s, br), 830 (s, br), 757 (s), 673 (s), 618 (m), 475 (w), 382 (m). Complete infrared spectrum, Figure A-10. Mass spectrum (70 eV), m/e (relative intensity, ion): 507 (9.2%, M), 492 (68.4%,  $\text{M} - \text{Me}$ ), 404 (33.6%,  $\text{M} - 2\text{Me} - \text{SiMe}_3$ ), 347 (47.2%,  $\text{M} - \text{N}(\text{SiMe}_3)_2$ ), 275 (70.2%,  $(\text{Me}_3\text{Si})_2\text{NAlNHSiMe}_3$ ), 202 (100%,  $(\text{Me}_3\text{Si})_2\text{NAlNH}$ ). Complete mass spectrum, Table A-6.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.24 ( $\text{CH}_3\text{Si}$ ).

#### Reaction of $\text{AlCl}_2\text{N}(\text{SiMe}_3)_2 \cdot \text{NEt}_3$ with $(\text{Me}_3\text{Si})_2\text{NH}$

A mixture of the complex (669.5 mg, 1.86 mmol) and  $(\text{Me}_3\text{Si})_2\text{NH}$  (1.20 g, 7.43 mmol) was heated in a sealed, evacuated ampoule at 110°C for 18.5 hr. No noncondensable volatiles were detected; the condensable volatiles (1.16 g) consisted essentially of  $(\text{Me}_3\text{Si})_2\text{NH}$  admixed with trace amounts of trimethylsilane and  $\text{Me}_3\text{SiCl}$ . The infrared spectrum of the residue was identical with that of the starting material,  $\text{AlCl}_2\text{N}(\text{SiMe}_3)_2 \cdot \text{NEt}_3$ .

#### Pyrolysis of $\text{AlCl}_2\text{N}(\text{SiMe}_3)_2 \cdot \text{NEt}_3$

The complex (491.6 mg, 1.37 mmol), was heated in an evacuated ampoule at 170°C for 17.5 hr. A total of 24.2 mg (0.24 mmol) of condensable volatiles was obtained; the major component was triethylamine admixed with traces of ethylene, trimethylsilane, and tetramethylsilane. A small quantity, ~0.13 mmol, of methane was produced. The residue, based on infrared spectral analysis, consisted largely of the starting material.

#### Pyrolysis of $\text{AlCl}[\text{N}(\text{SiMe}_3)_2]_2$

The chloro-compound (780.7 mg, 2.04 mmol) was heated in a sealed, evacuated ampoule at 150°C for 85.5 hr. The noncondensable volatiles consisted essentially of methane, 1.22 mmol; in the condensable volatiles,  $\text{Me}_3\text{SiCl}$  (0.11 mmol) was identified. The residue, a thick viscous liquid, was not characterized.

### Reaction of $[\text{AlCl}_2\text{NHSiMe}_3]_2$ with triethylamine

A mixture of  $[\text{AlCl}_2\text{NHSiMe}_3]_2$  (1.05 g, 2.82 mmol) triethylamine (0.58 g, 5.73 mmol), and toluene (5 mL) was stirred at room temperature for 16 hr in a closed system. Present in the condensable volatiles were triethylamine (2.37 mmol),  $(\text{Me}_3\text{Si})_2\text{NH}$  (1.36 mmol),  $\text{Me}_3\text{SiCl}$  (0.11 mmol), and toluene. The residue (1.14 g), a viscous liquid, was not characterized.

### Preparation of $[(\text{Me}_3\text{Si})_2\text{NAlNSiMe}_3]_2$

At room temperature, to a stirred solution of  $\text{LiN}(\text{SiMe}_3)_2$  (25.0 g, 149 mmol) in benzene (100 mL) was added  $[\text{AlCl}_2\text{NHSiMe}_3]_2$  (14.2 g, 38.1 mmol) in benzene (150 mL) over a period of 1.75 hr. After stirring for 24 hr, the precipitated  $\text{LiCl}$  (7.67 g) was filtered off. Removal of solvent in vacuo yielded 22.1 g of solid residue. Crystallization twice from Freon-113 gave 13.1 g (62.7% yield) of  $[(\text{Me}_3\text{Si})_2\text{NAlNSiMe}_3]_2$ , mp 192-194°C. Anal. Calcd for  $\text{C}_{18}\text{H}_{54}\text{Al}_2\text{N}_4\text{Si}_6$ : C, 39.37; H, 9.91; Al, 9.83; N, 10.20; MW, 549.14. Found: C, 38.98; H, 9.98; Al, 9.66; N, 10.6; MW, 600 (by vapor pressure depression at 0°C in pentane, 3.6 wt%). Infrared spectrum ( $\text{cm}^{-1}$ , KBr plates): 2951 (s), 2898 (m), 1440 (w), 1397 (w), 1252 (s), 1242 (s), 1017 (s, br), 963 (s, br), 901 (s, br), 827 (s, br), 771 (s), 753 (s), 695 (s), 672 (s), 629 (m), 612 (m), 477 (w), 365 (w). Complete infrared spectra, Figures A-11, A-12. MS (70 eV), m/e (relative intensity, ion): 548 (20.4%, M), 533 (100%, M - Me), 461 (22.0%, M -  $\text{NSiMe}_3$ ), 445 (24.2%, M -  $\text{SiMe}_3$  - 2Me), 373 (11.7%, M -



$\text{N}(\text{SiMe}_3)_2 - \text{Me}$ ). Complete mass spectrum, Table A-7.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  0.25 (18H,  $(\text{CH}_3)_3\text{Si}$ ), 0.28 (36H,  $[(\text{CH}_3)_3\text{Si}]_2\text{N}$ ).

Reaction of  $[(\text{Me}_3\text{Si})_2\text{NAlNSiMe}_3]_2$  with Ammonia

$[(\text{Me}_3\text{Si})_2\text{NAlNSiMe}_3]_2$  (10.10 g, 18.4 mmol) in hexane (48.68 g) was allowed to react with ammonia (0.67 g, 39.6 mmol) for 1 hr at  $0^\circ\text{C}$ . Specifically, using the vacuum line assembly, the measured quantity of ammonia, in an ampoule, was allowed to warm from  $-196^\circ\text{C}$  (by removing the liquid nitrogen trap) to room temperature, and as the ammonia was volatilized, it was absorbed by the reaction mixture held at  $0^\circ\text{C}$ . Subsequently, the reaction mixture was warmed to room temperature and stirred for 16 hr. The volatiles were removed in vacuo, initially at room temperature and finally at  $85^\circ\text{C}$ . The heating was necessary to remove the last traces of  $(\text{Me}_3\text{Si})_2\text{NH}$  and hexane. The volatile condensibles, in addition to hexane, consisted of ammonia (3.07 mmol, 7.7% recovery) and  $(\text{Me}_3\text{Si})_2\text{NH}$  (3.66 g, 22.7 mmol; 82.4% yield). The resultant solid was treated with Freon-113 (45 mL), and the small quantity of insoluble material was removed by filtration. The filtrate on evaporation gave 5.76 g (93% yield) of  $\text{Me}_3\text{SiNAl}(\text{NH}_2)\text{N}(\text{SiMe}_3)\text{AlNHSiMe}_3$  melting range  $195-215^\circ\text{C}$ . Anal. Calcd for  $\text{C}_9\text{H}_{30}\text{Al}_2\text{N}_4\text{Si}_3$ : C, 32.50; H, 9.09; Al, 16.23; N, 16.85; MW 332.59. Found: C, 31.27; H, 9.13; Al, 15.72; N, 16.90; MW 2300 (by vapor pressure depression in pentane, 3.4 wt%). Infrared spectrum ( $\text{cm}^{-1}$ , KBr plates): 3383 (m), 3330 (w), 3282 (m), 2947 (s), 2895 (m), 1435 (w, br), 1400 (w, br), 1250 (s), 1111 (s, br), 922 (s), 887 (s), 832 (s), 755 (s), 724 (m), 674

(m). Complete infrared spectrum, Figure A-13.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  -0.44 br (1H, NH), 0.22 s (9H,  $\text{CH}_3$ ), 0.35 s (9H,  $\text{CH}_3$ ), 0.40 s (9H,  $\text{CH}_3$ ), 0.87 br (2H,  $\text{NH}_2$ ). The TGA (to  $1000^\circ\text{C}$  at  $10^\circ\text{C}/\text{min}$ , in nitrogen atmosphere) showed a ceramic yield of 43.2%; calcd for pure AlN 24.65%.

Pyrolysis of  $\text{Me}_3\text{SiAl}(\text{NH}_2)\text{N}(\text{SiMe}_3)\text{AlNHSiMe}_3$

(1.84 g, 5.54 mmol) was heated in vacuo at  $200^\circ\text{C}$  for 24 hr; the volatiles evolved at this stage (175 mg) were composed of ammonia and  $(\text{Me}_3\text{Si})_2\text{NH}$ . Heating at  $278\text{--}280^\circ\text{C}$  for 21 hr gave an additional 280 mg of condensible volatiles for a total weight loss of 24.7%. The combined condensible volatiles were composed of  $(\text{Me}_3\text{Si})_2\text{NH}$  (3.18 mmol) and ammonia (0.63 mmol). Involatile residue infrared spectrum ( $\text{cm}^{-1}$ ): 3380 (w), 3295 (w), 2943 (s), 2890 (m), 1430 (w), 1400 (w), 1248 (s), 1107 (w), 1050 (w), 927 (s, br), 883 (s, br), 830 (s, br), 756 (s), 722 (m), 671 (m). Complete infrared spectrum, Figure A-14. A portion of the above product exhibited 32.5% weight loss under TGA condition; total weight loss (including the thermolysis at  $200\text{--}280^\circ\text{C}$ ) 51.7%. Calcd for pure AlN production, weight loss 75.35%. Another portion of the above thermolysis product (336.3 mg) was heated in a tube furnace in an ammonia atmosphere (500 mm Hg):  $280\text{--}540^\circ\text{C}$ , 0.3 hr;  $540\text{--}755^\circ\text{C}$ , 1.25 hr;  $755\text{--}990^\circ\text{C}$ , 1.5 hr. The residue was black and granular; ceramic yield 177.3 mg, 52.7%. Ceramic yield starting with  $\text{Me}_3\text{SiAl}(\text{NH}_2)\text{N}(\text{SiMe}_3)\text{AlNHSiMe}_3$  was 37.7%; calcd for pure AlN 24.65%.

### Reaction of $\text{Al}[\text{N}(\text{SiMe}_3)_2]_3$ and $\text{NH}_3$ in a 1:1 Ratio

Using a vacuum line, a stirred, degassed solution of  $\text{Al}[\text{N}(\text{SiMe}_3)_2]_3$  (2.08 g, 4.09 mmol) in heptane (18.33 g) was exposed at room temperature to ammonia (4.46 mmol) over a period of 21 hr. Specifically, the premeasured quantity of ammonia, in an ampoule, was allowed to warm slowly from  $-196^\circ\text{C}$  to room temperature, and as the ammonia was volatilized, it was absorbed by the reaction mixture. Thus, the pressure in the system never reached an atmosphere. After the 21 hr exposure, the volatiles, collected by evaporation in vacuo, consisted of heptane, hexamethyldisilazane (0.42 g, 2.60 mmol), and ammonia ( $<0.11$  mmol). From the involatile solid residue, the starting material was removed by sublimation in vacuo at  $110^\circ\text{C}$ . The sublimation residue (0.65 g, 43.6% yield, based on  $\text{Al}[\text{N}(\text{SiMe}_3)_2]_3$  originally employed) was crystallized from hexanes, producing fine, colorless needles of  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{AlNH}_2$ , mp  $219\text{--}221^\circ\text{C}$  (dec). DSC, Figure A-15. The material was stable in air. Anal. Calcd for  $\text{C}_{24}\text{H}_{76}\text{Al}_2\text{N}_6\text{Si}_8$ : C, 39.62; H, 10.53; Al, 7.42; N, 11.55; MW, 727.56. Found: C, 32.22; H, 9.61; Al, 7.08; N, 10.24; MW, 740 (by osmometry in benzene). Infrared spectrum ( $\text{cm}^{-1}$ , Kel-F/Nujol mull): 3415 (m, sh), 3396 (m, sh), 3357 (w), 3335 (w), 2948 (m), 2899 (w), 1263 (s), 1246 (s), 920 (s, br), 873 (s, br), 852 (s, br), 835 (s, br), 757 (m), 671 (s), 619 (m). Complete infrared spectrum, Figure A-16. Mass spectrum (70 eV) m/e (relative intensity, ion): 726 (9%, M), 711 (28%, M - Me), 550 (100%, M - Me -  $(\text{Me}_3\text{Si})_2\text{NH}$ ), 348 (53%,  $(\text{Me}_2\text{Si})\text{Me}_3\text{SiNAlN}(\text{SiMe}_3)_2\text{NH}_2$ ), 275 (51%,  $(\text{Me}_3\text{Si})_2\text{NAl}(\text{NH}_2)\text{NSiMe}_2$ ), 203 (30%,  $(\text{Me}_3\text{Si})_2\text{NAlNH}_2$ ), 146

(67%, (Me<sub>2</sub>Si)Me<sub>3</sub>SiNH), 130 (44%, (MeSi)Me<sub>3</sub>SiN), 73 (53%, Me<sub>3</sub>Si). Complete mass spectrum, Table A-8. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 0.47 (Me<sub>3</sub>Si, 36H), 1.75 (NH, 2H).

Reaction of Al[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub> and NH<sub>3</sub> in a 1:2 Ratio

A stirred, degassed solution of Al[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub> (9.73 g, 19.1 mmol) in heptane (76.77 g) was exposed at room temperature to ammonia (38.5 mmol) over a period of 18 hr. The volatiles collected by evaporation in vacuo consisted of heptane, hexamethyldisilazane (4.30 g, 27.2 mmol), and ammonia (0.93 mmol). The residue was recrystallized from benzene, resulting in the isolation of 3.31 g (59.3% yield) of colorless prisms of [(Me<sub>3</sub>Si)<sub>2</sub>N]<sub>2</sub>Al(NH<sub>2</sub>)<sub>2</sub>]<sub>3</sub>Al, mp 191°C (dec). DSC, Figure A-17. Anal. Calcd for C<sub>36</sub>H<sub>120</sub>Al<sub>4</sub>N<sub>12</sub>Si<sub>12</sub>: C, 37.07; H, 10.37; Al, 9.25; N, 14.41; MW, 1166.40. Found: C, 39.01; H, 10.55; Al, 9.69; N, 14.50; MW (by osmometry in benzene) 1150. Infrared spectrum (cm<sup>-1</sup>, Kel-F/Nujol mull): 3410 (s), 3330 (m), 2943 (s), 2895 (m), 1477 (m), 1436 (m), 1400 (m), 1262 (s), 1247 (s), 920 (s, br), 872 (s, br), 822 (s, br), 760 (s), 720 (m), 672 (s), 637 (s), 603 (m). Complete infrared spectrum, Figure A-18. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 1.50, 1.44 (NH, 6H); 0.82, 0.76 (NH, 6H); 0.45, 0.37 (Me<sub>3</sub>Si, 108H). The TGA (to 1000°C at 10°C/min in nitrogen atmosphere) showed a ceramic yield of 24.1%, which is higher than the 14.1% calcd for pure AlN.

Low Temperature Pyrolysis of [(Me<sub>3</sub>Si)<sub>2</sub>N]<sub>2</sub>AlNH<sub>2</sub>]<sub>2</sub>

A 366.7 mg (0.504 mmol) sample was heated in an evacuated ampoule at 225°C for 16 hr. After cooling to room

temperature, the volatiles were collected and quantified:  
(Me<sub>3</sub>Si)<sub>2</sub>NH, 1.10 mmol. The white solid (189 mg) remaining in the tube was found to be soluble in hexane, benzene, and ether.  
Anal. Calcd for C<sub>24</sub>H<sub>76</sub>Al<sub>4</sub>N<sub>8</sub>Si<sub>8</sub>: C, 35.61; H, 9.46; Al 13.33; N, 13.84; MW, 809.51. Found: C, 30.54; H, 8.35; Al, 14.69; N, 11.62; MW, 790 (by vapor pressure depression in pentane).  
Infrared spectrum (cm<sup>-1</sup>, Kel-F/Nujol mull): 3376 (w), 2947 (m), 2892 (w), 1257 (s), 1063 (w, br), 937 (s, br), 892 (s), 841 (s), 760 (m), 730 (m), 677 (m), 618 (w). Complete infrared spectrum, Figure A-19. <sup>1</sup>H NMR: δ 0.35 (Me<sub>3</sub>Si, 72H); 0.09 (NH, 4H).  
Attempts at crystallization were unsuccessful. The TGA (to 1000°C at 10°C/min in nitrogen atmosphere) showed a ceramic yield of 53.8%, which is higher than the 20.23% calcd for pure AlN.

#### Pyrolysis of [(Me<sub>3</sub>Si)<sub>2</sub>NAlNH]<sub>4</sub>

In vacuo an 80 mg (0.099 mmol) sample was gradually heated from room temperature to 900°C over a period of 4 hr; a black residue remained, showing carbon retention. The volatiles were collected and quantified: CH<sub>4</sub>, 0.67 mmol; (Me<sub>3</sub>Si)<sub>2</sub>NH, 0.05 mmol. A white sublimate, determined by infrared analysis to be [(Me<sub>3</sub>Si)<sub>2</sub>NAlNH]<sub>4</sub>, was deposited on the walls of the quartz tube outside the heated zone.

#### Pyrolysis of [(Me<sub>3</sub>Si)<sub>2</sub>NAlNH]<sub>4</sub> in an Ammonia Atmosphere.

A 128.2 mg sample was heated in a tube furnace in an ammonia atmosphere (500 mm Hg) under the following conditions: 25-310°C 5 hr; 310°C 14.5 hr; 310-770°C 2.5 hr; 770-980°C 1.5 hr. A black residue (74.4 mg) was obtained, corresponding to a

ceramic yield of 58%, which is higher than the 20.23% calcd for pure AlN.

Pyrolysis of  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\text{NH}_2)_2\text{Al}$ .

$[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\text{NH}_2)_2\text{Al}$  (713.9 mg, 0.612 mmol) was weighed into a 20 mL ampoule, which was evacuated, sealed, and placed in an oven at 200°C for 16 hr. After the tube had cooled to room temperature, the volatiles were collected and quantified:  $(\text{Me}_3\text{Si})_2\text{NH}$ , 3.09 mmol. The white solid remaining in the tube was found to be insoluble in hexane, benzene, and ether. Anal. Calcd for  $\text{C}_6\text{H}_{25}\text{Al}_4\text{N}_7\text{Si}_2$ : C, 20.05; H, 7.01; Al, 30.02; N, 27.28. Found: C, 16.85; H, 6.61; Al, 30.32; N, 14.35. Infrared spectrum ( $\text{cm}^{-1}$ , Kel-F/Nujol mull): 2945 (w), 1245 (m), 905 (s, br), 830 (s, br), 753 (s, br), 673 (s, br). A portion of the solid (173.3 mg) was transferred to a quartz tube, which was evacuated and heated from room temperature to 900°C over a period of 3 hr. A white solid residue remained; the volatiles were collected and quantified:  $\text{CH}_4$ , 2.24 mmol;  $\text{NH}_3$ , 0.25 mmol;  $(\text{Me}_3\text{Si})_2\text{NH}$ , 0.03 mmol. A portion of the low temperature thermolysis product was heated to 1000°C over 8 hr in flowing  $\text{N}_2$  (0.2-0.3 standard cubic feet per hour (SCFH)) and held at 1000°C for 8 hr. This was followed by heating to 1600°C over 4 hr and 4 hr residence at the temperature.

Another portion of the low temperature thermolysis product was heated from room temperature to 1000°C over a period of 8 hr, followed by an additional 8 hr at 1000°C in a horizontal quartz furnace tube under ammonia flow (0.2-0.3 SCFH).

Interaction of  $\text{AlCl}[\text{N}(\text{SiMe}_3)_2]_2$  with ammonia

a) At 0°C in a sealed ampoule

A solution of  $\text{AlCl}[\text{N}(\text{SiMe}_3)_2]_2$  (9.24 g, 24.37 mmol) in toluene (9.61 g) was treated with ammonia (49.20 mmol) in an evacuated, sealed ampoule at -78°C for 16 hr, 0°C for 16 hr, and at room temperature for ~2 hr. Opening to a vacuum system and fractionation from a warming trap through traps cooled to -47, -78, and -196°C resulted in recovery of 1.94 mmol of ammonia (indicating 97% completion of the expected process) and collection of 4.27 g (26.52 mmol) of hexamethyldisilazane (determined from weight increase in the toluene fraction and confirmed by quantitative gas chromatography). The involatile residue was extracted with pentane followed by boiling benzene. The insoluble residue (2.38 g;  $\text{NH}_4\text{Cl}$  expected, 1.30 g), based on infrared spectral analysis, contained ammonium chloride admixed with trimethylsilyl-substituted material. On sublimation, 966 mg, 74%, of ammonium chloride was obtained. Inasmuch as during the sublimation ammonia (266 mg, 15.6 mmol) and hexamethyldisilazane (280 mg, 1.7 mmol) were collected, it is possible that at least some of the ammonia was derived from ammonium chloride dissociation. The pentane soluble portion was crystallized from pentane giving 1.23 g (13.4% yield of  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{AlNH}_2$ ) of white crystals. Sublimation at 135°C afforded 40 mg of material. The residue, mp 234-235°C, gave essentially an identical mass spectrum as  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{AlNH}_2$ . Attempts at purification of the material (2.10 g) left on solvent evaporation failed to result in isolation of any pure product. Heating to 105°C

resulted in hexamethyldisilazane evolution and sublimation of material which exhibited a mass spectrum essentially identical with that given in Table A-9.

b) At -20°C in a vacuum line system

Using a vacuum line, a stirred, degassed solution of  $\text{AlCl}[\text{N}(\text{SiMe}_3)_2]_2$  (7.32 g, 19.1 mmol) in hexanes (16.54 g) was exposed at -20°C to ammonia (38.7 mmol) over a period of 1 hr. After the reaction mixture was stirred for 16 hr at 0°C, a fine precipitate (1.65 g) was filtered off. Removal of solvent from the filtrate in vacuo yielded 3.21 g of a white solid. Recrystallization from Freon-113 gave 1.37 g of a low melting solid, mp 81-83°C. Anal. found: C, 36.18; H, 10.22; Al, 9.11; N, 10.05; Si, 18.84; MW 910 (by vapor pressure depression at 0°C, 4.1 wt%). Infrared spectrum ( $\text{cm}^{-1}$ , Kel-F/Nujol mull): 3403 (s), 3339 (m), 2943 (s), 2895 (s), 1402 (w), 1264 (s), 1250 (s), 1200 (m, sh), 930 (s), 880 (s), 830 (s), 758 (s), 692 (s), 673 (s), 640 (s), 618 (m). Complete infrared spectrum, Figure A-20; DSC, Figure A-21; mass spectrum, Table A-9.

Preparation of  $\text{Et}_3\text{N} \cdot \text{Cl}_2\text{AlN}(\text{SiMe}_3)\text{B}(\text{NH}_2)\text{NHSiMe}_3$

A mixture of  $\text{Me}_3\text{SiAl}(\text{NH}_2)\text{N}(\text{SiMe}_3)\text{AlNHSiMe}_3$  (2.09 g, 6.29 mmol), triethylamine (1.31 g, 12.94 mmol), and  $(\text{Me}_3\text{Si})_2\text{NBClNHSiMe}_3$  (7.33 g, 24.87 mmol) was heated in an evacuated, sealed ampoule at 63-67°C for 24 hr. During that period deposition of a solid was observed. Following the removal in vacuo of room temperature volatiles, the residue was treated with pentane (in an inert atmosphere enclosure) yielding 3.85 g



(76.4% yield) of a white, benzene soluble, solid. Analysis of the residue Calcd for  $C_{12}H_{36}AlBCl_2N_4Si_2$ : C, 35.91; H, 9.04; N ( $NH_3$ ), 10.47; Cl, 17.70; B, 2.74, Al, 6.72. Found: C, 35.82; H, 9.45; N ( $NH_3$ ), 10.7; Cl, 17.8; B, 2.65; Al, 5.49. Infrared spectrum, Figure A-22; DSC, Figure A-23. TGA (nitrogen) residue 16.2%; Calcd for  $AlNBN$ : 16.16%.

Pyrolysis of  $Et_3N \cdot Cl_2AlN(SiMe_3)B(NH_2)NHSiMe_3$

A sample of  $Et_3N \cdot Cl_2AlN(SiMe_3)B(NH_2)NHSiMe_3$  (0.52 g, 1.30 mmol) was heated in a tube furnace under vacuum for 16 hr at 300-330°C. The volatile condensibles (0.23 g) consisting of triethylamine and trimethylchlorosilane were removed and the quartz tube was filled with 500 mm of ammonia. The tube was then heated under the following conditions: 25-330°C 1 hr; 330-880°C 2.5 hr; 880-1010°C 1 hr. The volatile condensibles consisted of hexamethyldisilazane and  $(Me_3Si)_2NB(NH_2)NHSiMe_3$ . On the inner walls of the quartz tube above the heated zone was sublimed a white solid which was identified by infrared spectroscopy as ammonium chloride. The brown solid residue (0.08 g, 15.4%) was subjected to thermogravimetric analysis in nitrogen up to 1000°C producing a white solid (10.9% wt. loss) which was determined by X-ray powder diffraction to be a mixture of  $AlN$  and  $BN$ . Infrared spectrum, Figure A-24.

Interaction of  $Et_3N \cdot Cl_2AlN(SiMe_3)B(NH_2)NHSiMe_3$  with the lithium salt of hexamethyldisilazane

a) In a 1:1 mole ratio

To a stirred solution of  $\text{Et}_3\text{N} \cdot \text{Cl}_2 \cdot \text{AlN}(\text{SiMe}_3)\text{B}(\text{NH}_2)\text{NHSiMe}_3$  (1.00 g, 2.49 mmol) in benzene (5 ml) was added the lithium salt of hexamethyldisilazane (0.42 g, 2.51 mmol) in benzene (5 ml) over a period of 30 min. After the reaction mixture was stirred at room temperature for 140 hr, the insoluble solid (0.09 g) was filtered off. Removal of the volatiles from the filtrate in vacuo resulted in the recovery of 0.98 g of solid. Hexamethyldisilazane (2.03 mmol) and triethylamine (0.26 mmol) were found in the volatiles; the major component was benzene. The solid was recrystallized from hexanes giving 0.26 g (25% yield) of colorless crystals mp 151-156°C. Anal. Calcd for  $(\text{Me}_3\text{Si})_2\text{NAl}(\text{Cl})\text{N}(\text{SiMe}_3)\text{B}(\text{NH}_2)\text{NHSiMe}_3$ ,  $\text{C}_{12}\text{H}_{39}\text{AlBClN}_4\text{Si}_4$ : C, 33.91; H, 9.25; Al, 6.35; B, 2.54; Cl, 8.34; N, 13.18; Si, 26.43. Found: C, 39.14; H, 9.92; Al, 2.23; B, 1.14; Cl, 9.64; N, 10.90; Si, 23.91. IR, Figure A-25; DSC, Figure A-26; TGA, Figure A-27. Weight loss TGA, 84.1%, Calcd for  $\text{AlNBN}$ , 84.5%.

b) In a 1:2 mole ratio

To a stirred solution of  $\text{Et}_3\text{N} \cdot \text{Cl}_2 \cdot \text{AlN}(\text{SiMe}_3)\text{B}(\text{NH}_2)\text{NHSiMe}_3$  (0.92 g, 2.29 mmol) in benzene (5 ml) was added the lithium salt (0.78 g, 4.66 mmol) in benzene (10 ml). After the reaction mixture was stirred for 168 hr at room temperature, the insoluble solid (0.12 g) was filtered off. Evaporation of the filtrate in vacuo gave in the condensable volatiles benzene, hexamethyldisilazane (1.33 mmol) and triethylamine (0.08 mmol). The solid residue, 1.22 g, was treated with hexane; all but 0.05 g dissolved. After the removal of hexane from the filtrate the involatile amber solid was crystallized from Freon-113, affording

0.44 g (35% yield) of a white material, mp 177-186°C. Anal. Calcd for  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{AlN}(\text{SiMe}_3)\text{B}(\text{NH}_2)\text{NHSiMe}_3$ ,  $\text{C}_{18}\text{H}_{57}\text{AlBN}_5\text{Si}_6$ : C, 39.31; H, 10.45; Al, 4.91; B, 1.97; N, 12.73; Si, 30.64. Found: C, 38.77; H, 10.30; Al, 4.49; B, 1.70; N, 10.49; Si, 32.71. IR, Figure A-28; DSC, Figure A-29; TGA, Figure A-30. Weight loss TGA, 88.12%. Calcd for  $\text{AlNBN}$ , 88.04%.

Interaction of boron trichloride with tris[bis(trimethylsilyl)amino]aluminum

a) In heptane at room temperature

A mixture of tris[bis(trimethylsilyl)amino]aluminum (268.7 mg, 0.529 mmol), boron trichloride (97 mg, 0.826 mmol), and heptane (8 ml) was stirred at room temperature for 64 hr. On volatiles removal, pure starting material, tris[bis(trimethylsilyl)amino]aluminum, was recovered.

b) In heptane at 51°C for 15 hr

A mixture of tris[bis(trimethylsilyl)amino]aluminum (166.4 mg, 0.328 mmol) and boron trichloride (67.5 mg, 0.576 mmol) was heated in heptane (4.499 g) in a sealed, evacuated ampoule at 51°C for 15 hr. No reaction occurred as determined by the complete recovery of the starting materials.

c) In heptane at 71°C for 73 hr

Heating the above mixture at 71°C for 73 hr in a sealed ampoule resulted in the formation of trimethylboron (0.09 mmol), tetramethylsilane (0.14 mmol), and trimethylchlorosilane (0.12 mmol). If one assumes boron to substitute for silicon, then 0.25

mmol of boron was incorporated, which corresponds to 44% of the available boron.

d) At 100°C in the absence of solvent

A mixture of tris[bis(trimethylsilyl)amino]aluminum (260 mg, 0.513 mmol) and boron trichloride (85.0 mg, 0.726 mmol) was heated in vacuo in a sealed ampoule at 100°C for 24 hr. The volatiles produced were fractionated using a vacuum system from a warming trap through -96°C into a liquid nitrogen cooled trap. The condensible volatiles consisted of trimethylboron (0.11 mmol), tetramethylsilane (0.64 mmol), and trimethylchlorosilane (0.17 mmol). The involatile residue was in the form of a thick, viscous liquid. It exhibited an infrared spectrum completely different from that of the starting material.

Interaction of B-trichloroborazine with tris[bis(trimethylsilyl)amino]aluminum

a) In benzene/hexane at room temperature

A mixture of B-trichloroborazine (0.50 g, 2.72 mmol) and tris[bis(trimethylsilyl)amino]aluminum (1.38 g, 2.72 mmol) was stirred in a solution of benzene (10 ml) and hexane (2 ml) at room temperature for 16 hr. Removal of the volatiles from the reaction mixture resulted in a solid (1.65 g) which was found to be a mixture of the starting materials. Analysis of the volatile condensibles showed the presence of benzene and hexanes; only a trace amount of trimethylchlorosilane was observed.

b) In toluene at 100°C

A mixture of B-trichloroborazine (414.1 mg, 2.25 mmol), tris[bis(trimethylsilyl)amino]aluminum (1218.8 mg, 2.40 mmol), and toluene (2850.2 mg) was heated in an evacuated sealed ampoule at 103°C for 15 hr. The condensible volatiles consisted mainly of toluene and trimethylchlorosilane (2.12 mmol). The product could not be separated from the starting materials in the yellow solid residue.

Interaction of tris[bis(trimethylsilyl)amino]aluminum and bis(trimethylsilyl)amino dichloroborane

a) In heptane

A mixture of tris[bis(trimethylsilyl)amino]aluminum (505.8 mg, 0.995 mmol), bis(trimethylsilyl)amino dichloroborane (231.1 mg, 0.954 mmol), and heptane (2953.8 mg) was heated in an evacuated sealed ampoule at 75°C for 19.5 hr. Upon opening to the vacuum system, the condensible volatiles were collected. These volatiles consisted mainly of heptane with a small amount of the dichloroborane starting material. The infrared spectrum of the residue showed the presence of both starting materials.

b) Neat

A mixture of tris[bis(trimethylsilyl)amino]aluminum (502.0 mg, 0.988 mmol) and bis(trimethylsilyl)amino dichloroborane (257.8 mg, 1.070 mmol) was heated in vacuo in a sealed ampoule at 100°C for 24 hr. The condensible volatiles consisted mainly of trimethylchlorosilane (0.23 mmol). The recovery of starting materials in the residue indicates that the trimethyl-

chlorosilane was formed by the partial pyrolysis of the dichloroborane.

Interaction of  $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Al}$  with aminobis(trimethylsilyl)aminotrimethylsilylaminoborane

A mixture of  $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Al}$  (500 mg, 0.98 mmol) and  $(\text{Me}_3\text{Si})_2\text{NB}(\text{NH}_2)\text{NHSiMe}_3$  (300 mg, 1.09 mmol) was heated in a nitrogen atmosphere at 100°C for 4 hr. The infrared spectrum of the heat treated material showed the presence of both starting materials; no additional bands were observed, indicating an absence of reaction.

Interaction of  $\text{AlCl}_3 \cdot \text{NEt}_3$  with aminobis(trimethylsilyl)aminotrimethylsilylaminoborane

A solution of the adduct,  $\text{AlCl}_3 \cdot \text{NEt}_3$  (630 mg, 2.69 mmol) in benzene (3.33 g) was stirred with  $(\text{Me}_3\text{Si})_2\text{NB}(\text{NH}_2)\text{NHSiMe}_3$  (790 mg, 2.87 mmol) in an inert atmosphere enclosure at room temperature for 12 hr. No change in appearance was noted. Subsequently, the solution was heated in a closed system at 85°C for 91 hr. No precipitate was deposited on the walls of the connecting apparatus. The volatile condensibles contained 320 mg (1.99 mmol) of hexamethyldisilazane. The involatile residue was extracted with pentane. The pentane soluble portion (350 mg, 1.01 mmol) was composed essentially of  $(\text{Me}_3\text{Si})_2\text{NB}(\text{NH}_2)\text{N}(\text{SiMe}_3)_2$ , as determined by GC/MS; no starting material was recovered. No triethylamine hydrochloride, based on infrared analysis, was present in the residue.

Interaction of  $(\text{Me}_3\text{Si})_2\text{NAlCl}_2 \cdot \text{NEt}_3$  with aminobis(trimethylsilyl)aminotrimethylsilylaminoborane

In an inert atmosphere enclosure  $(\text{Me}_3\text{Si})_2\text{NAlCl}_2 \cdot \text{NEt}_3$  (350.5 mg, 0.975 mmol) and aminobis(trimethylsilyl)aminotrimethylsilylaminoborane (420.6 mg, 1.527 mmol) were placed in an ampoule and allowed to stir at room temperature for 72 hr. A small amount of solid was deposited; it was not triethylamine hydrochloride. The ampoule was sealed in vacuo and then was heated at 67°C for 15.5 hr. During that time a white solid admixed with a brown oil was formed. On opening to the vacuum system 0.135 mmol of a 1:1 mixture of triethylamine and hexamethyldisilazane was observed. The residue was extracted with pentane giving 400 mg of soluble material which, based on GC/MS, consisted of a 1:1 mixture of  $(\text{Me}_3\text{Si})_2\text{NB}(\text{NH}_2)\text{NHSiMe}_3$  and  $(\text{Me}_3\text{Si})_2\text{NB}(\text{NHSiMe}_3)_2$ . The pentane insoluble solid (60 mg) did not contain triethylamine hydrochloride; it exhibited a spectrum different from  $(\text{Me}_3\text{Si})_2\text{NAlCl}_2 \cdot \text{NEt}_3$ .

Interaction of  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\text{NH}_2)_2]_3\text{Al}$  with bis(trimethylsilyl)aminotrimethylsilylaminochloroborane and triethylamine

A mixture of  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\text{NH}_2)_2]_3\text{Al}$  (470.7 mg, 0.4035 mmol), bis(trimethylsilyl)aminotrimethylsilylaminochloroborane (499.6 mg, 1.694 mmol), and triethylamine (236.3 mg, 2.335 mmol) was heated in an evacuated, sealed ampoule for 22 hr at 62°C and for 16.5 hr at 77°C. The volatile condensibles (240.9 mg) consisted mainly of triethylamine with small amounts of

hexamethyldisilazane and trimethylchlorosilane. The residue was put into pentane, and the insoluble portion was filtered off. This insoluble solid (0.25 g) was found to be mainly  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\text{NH}_2)_2]_3\text{Al}$ . The pentane soluble material (0.47 g) was a mixture of the aluminum and boron starting materials.

Interaction of  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\text{NH}_2)_2]_3\text{Al}$  with bis(trimethylsilyl)amino dichloroborane and triethylamine

A mixture of  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\text{NH}_2)_2]_3\text{Al}$  (480.2 mg, 0.4117 mmol), bis(trimethylsilyl)aminodichloroborane (429.5 mg, 1.774 mmol), and triethylamine (236.3 mg, 2.335 mmol) was heated in an evacuated, sealed ampoule for 22 hr at 62°C and for 16.5 hr at 77°C. The condensible volatiles (200.3 mg) consisted mainly of triethylamine with small amounts of trimethylchlorosilane and hexamethyldisilazane. The pentane insoluble portion (0.21 g) of the residue was determined to be  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\text{NH}_2)_2]_3\text{Al}$ . The pentane soluble material (0.55 g) was a mixture of  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\text{NH}_2)_2]_3\text{Al}$  and  $(\text{Me}_3\text{Si})_2\text{NBCl}_2$ .

Interaction of  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\text{NH}_2)_2]_3\text{Al}$  with B-trichloroborazine and triethylamine

A mixture of  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\text{NH}_2)_2]_3\text{Al}$  (499.7 mg, 0.4284 mmol), B-trichloroborazine (269.3 mg, 1.465 mmol), and triethylamine (217.5 mg, 2.149 mmol) was heated in an evacuated, sealed ampoule at 77°C for 16.5 hr. The volatile condensibles (61.8 mg) consisted mainly of triethylamine (0.61 mmol). The residue was treated with hot benzene, and the insoluble solid was



filtered off. This solid (0.41 g) was identified by infrared spectral analysis as a mixture of triethylamine hydrochloride and chloroborazine or its derivative. Removal of benzene from the filtrate resulted in a solid (510 mg), which, based on infrared spectral analysis, consisted mainly of  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\text{NH}_2)_2]_3\text{Al}$ , plus a small amount of  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{AlNH}_2]_2$ .

Interaction of triphenylphosphine, lithium azide, and  $[\text{AlCl}_2\text{NHSiMe}_3]_2$  in acetonitrile

Under nitrogen bypass, into a stirred mixture of triphenylphosphine (170 mg, 0.65 mmol) and lithium azide (30 mg, 0.61 mmol) in acetonitrile (5 ml) was added at room temperature  $[\text{AlCl}_2\text{NHSiMe}_3]_2$  (50 mg, 0.27 mmol) in acetonitrile (2 ml). The infrared spectrum of the reaction mixture taken after 1.7 hr showed a very strong band at  $2120\text{ cm}^{-1}$  (absent in the lithium azide/triphenylphosphine/acetonitrile mixture). After heating at  $90\text{--}96^\circ\text{C}$  for 27 hr, the azide band decreased; however, no P-N bands appeared. The precipitated solid, based on its infrared spectrum, appeared to be an aluminum azide admixed with triphenylphosphine.

Interaction of phosphorus trichloride and tris[bis(trimethylsilyl)amino]aluminum

A mixture of tris[bis(trimethylsilyl)amino]aluminum (504.1 mg, 0.992 mmol), phosphorus trichloride (149.2 mg, 1.086 mmol), and heptane (5 ml) was stirred under vacuum at room temperature for 16 hr. The volatiles were fractionated using the vacuum system from a warming trap through  $-47$  and  $-63^\circ\text{C}$  held

traps into a liquid nitrogen cooled trap. These volatiles consisted of heptane, phosphorus trichloride and a trace of trimethylchlorosilane. The infrared spectrum of the white solid residue indicated the presence of essentially pure tris[bis(trimethylsilyl)amino]aluminum.

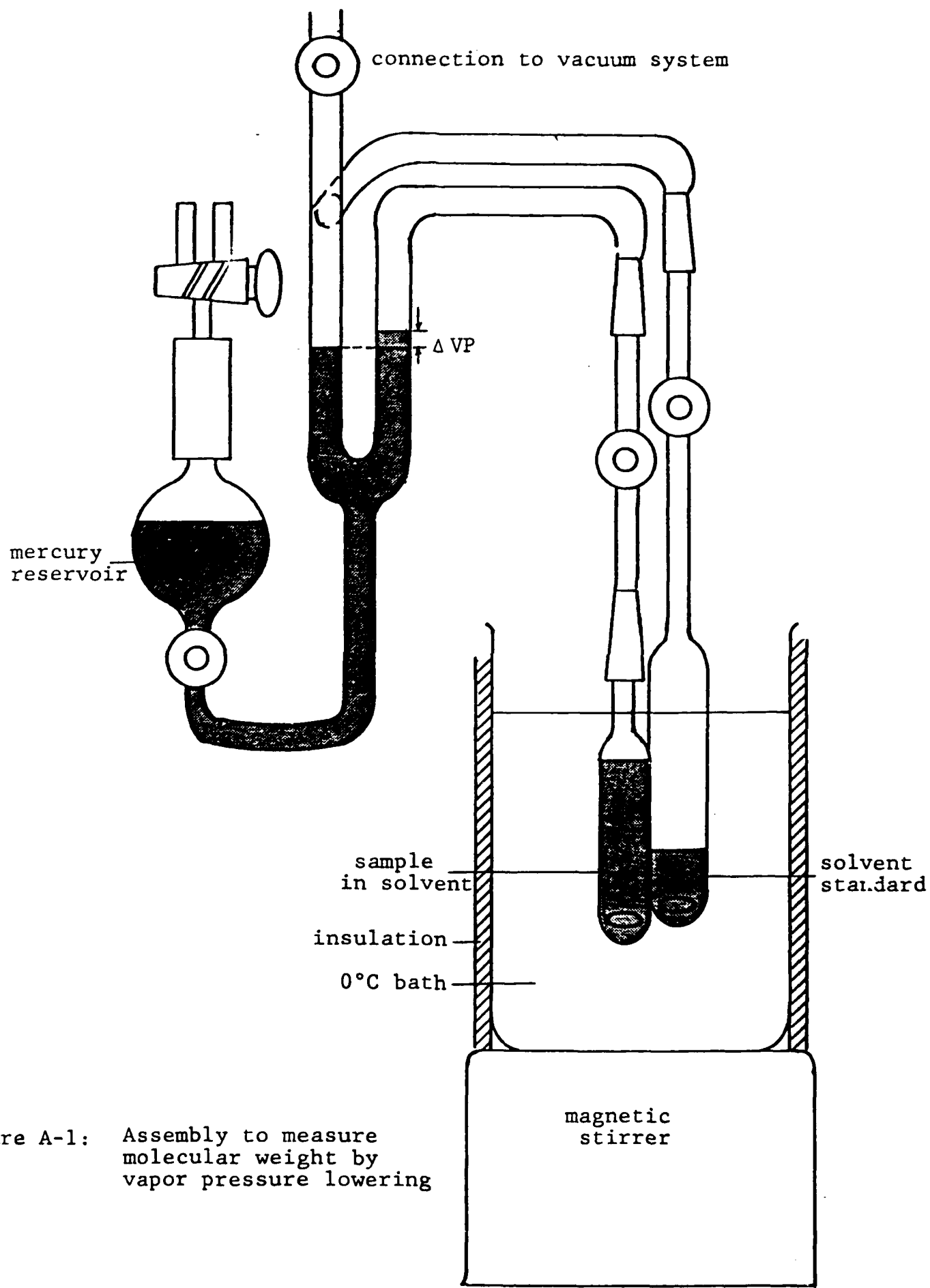


Figure A-1: Assembly to measure molecular weight by vapor pressure lowering

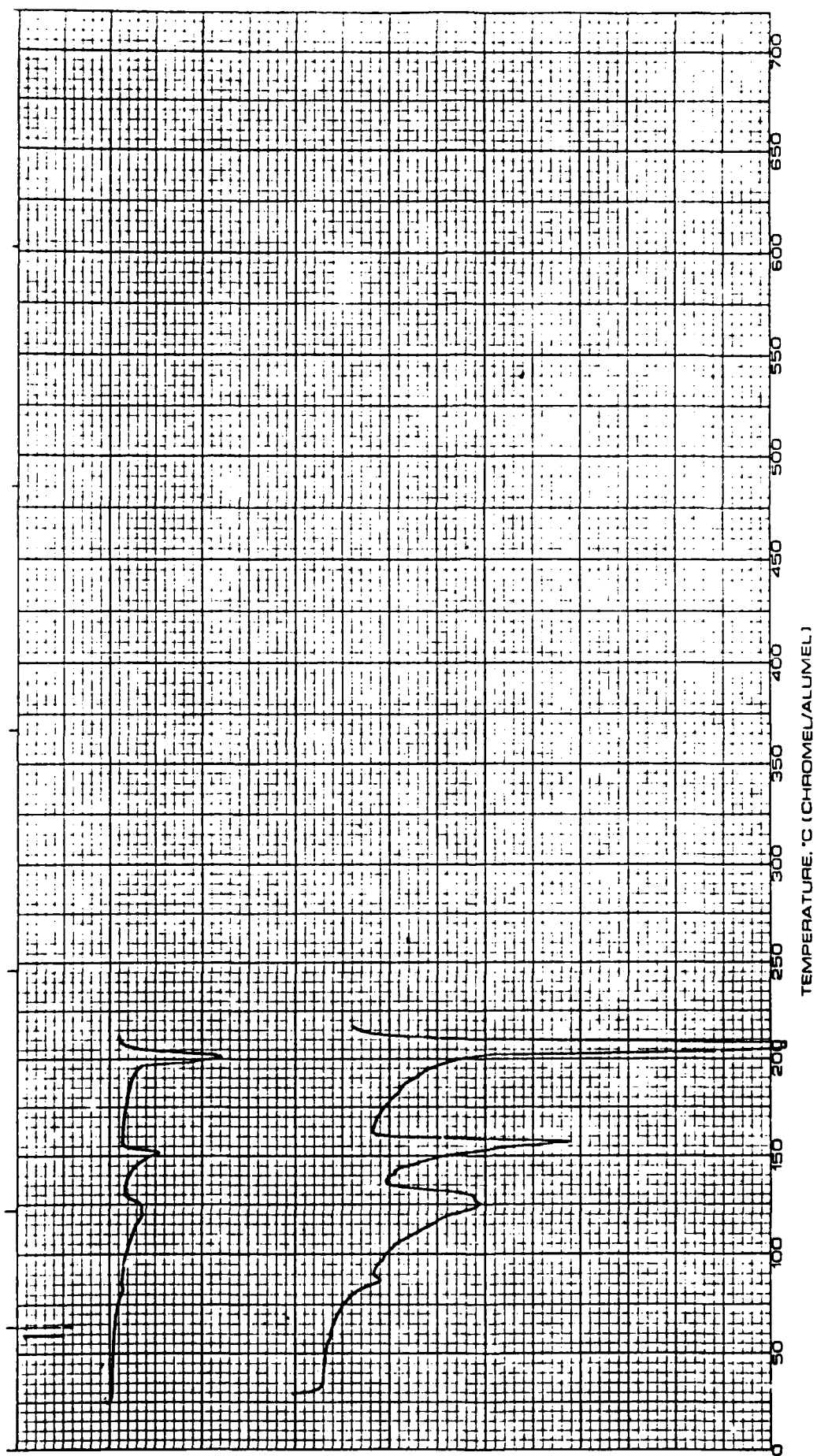


Figure A-2: DSC scan of the adduct  $\text{AlCl}_3 \cdot \text{NH}(\text{SiMe}_3)_2$ .

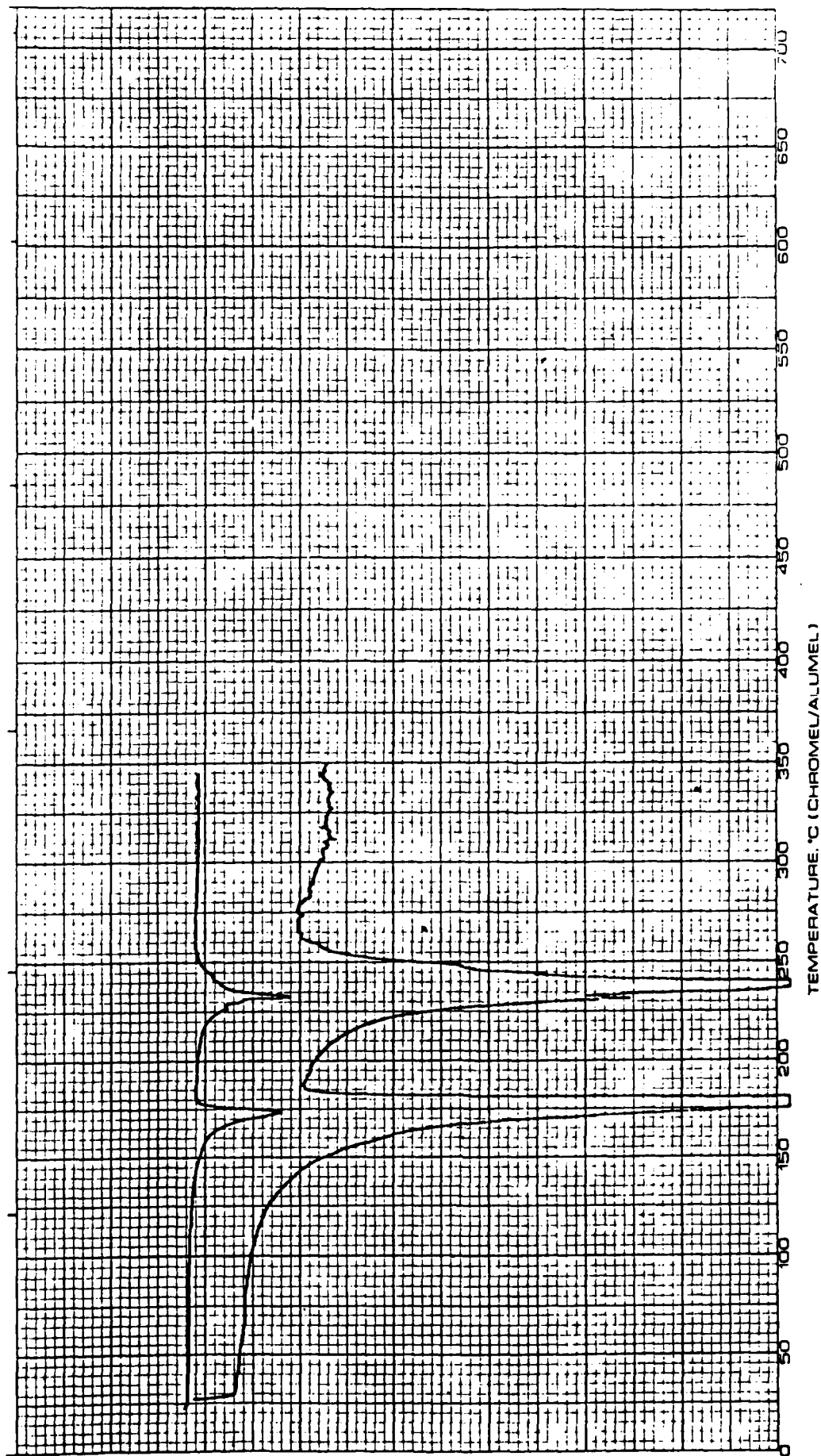


Figure A-3: DSC scan of  $[\text{AlCl}_2\text{NHSiMe}_3]_2$ .

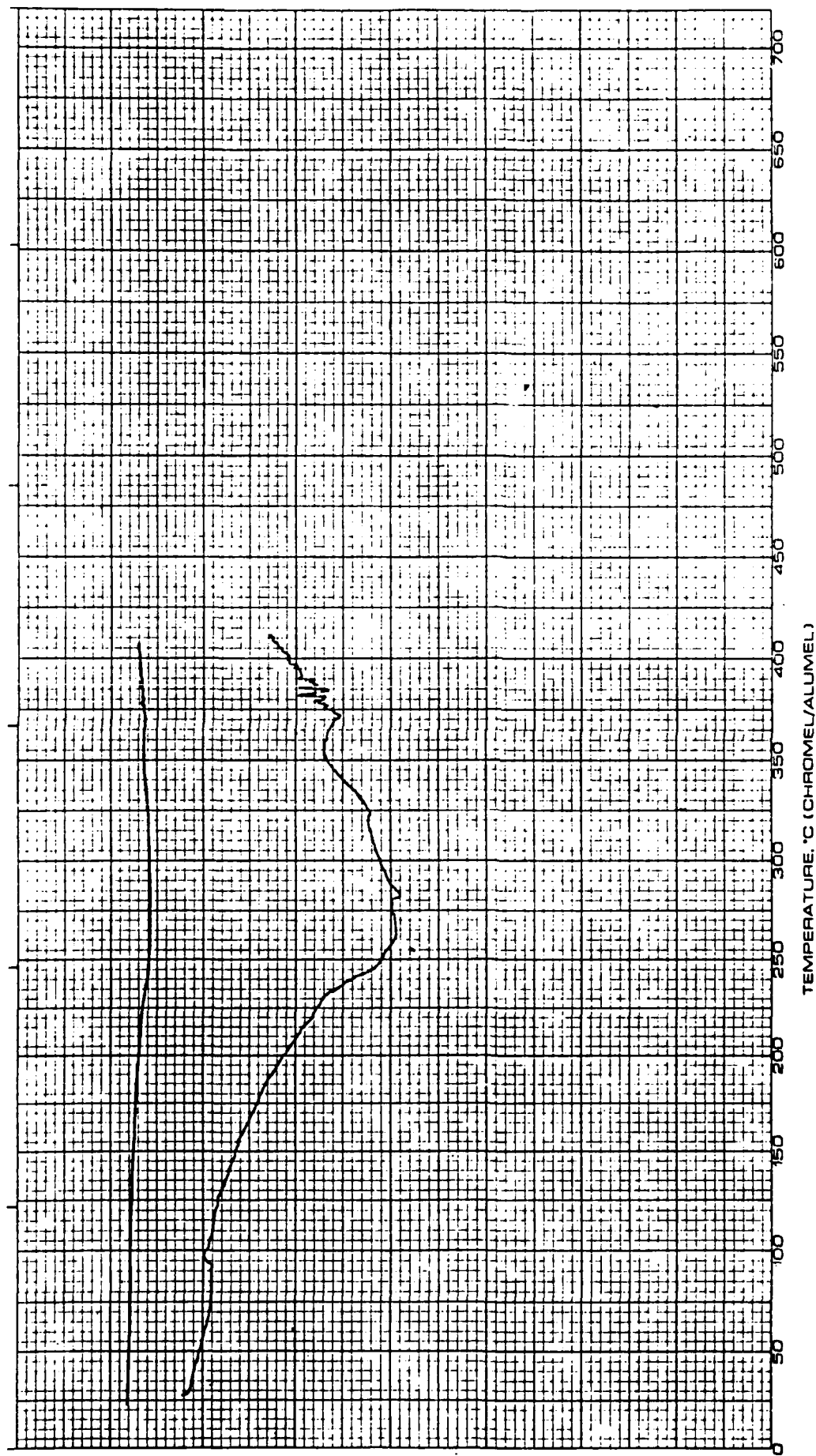


Figure A-4: DSC scan of  $[\text{AlClNH}]_3\text{AlCl}_2\text{NHSiMe}_3$ .

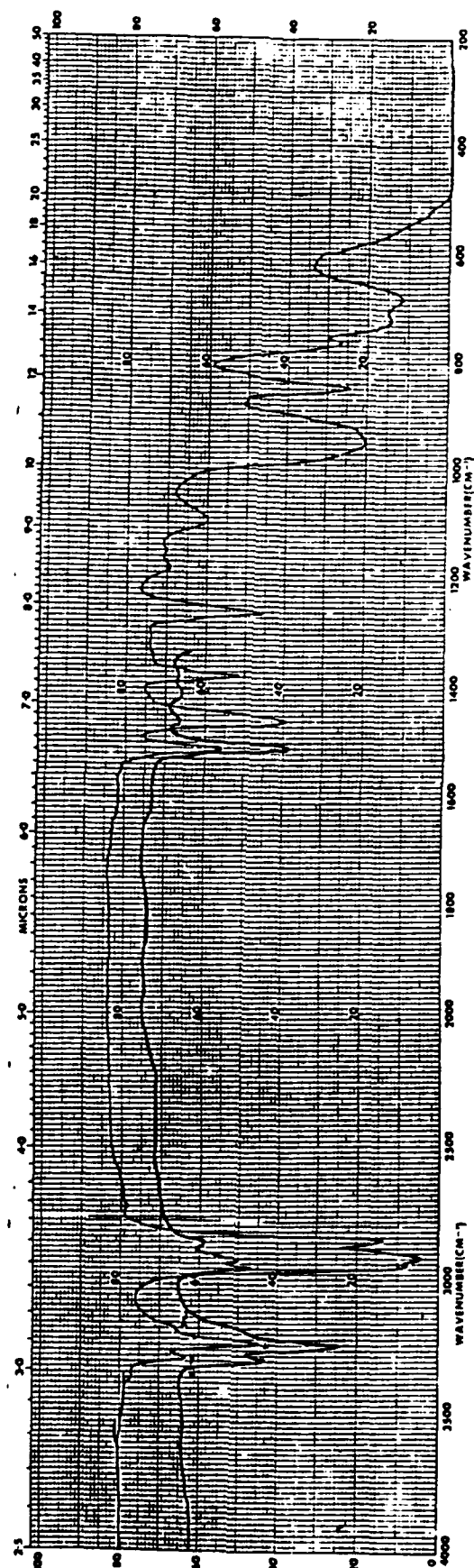


Figure A-5: Infrared spectrum of  $[\text{AlClNH}]_3\text{AlCl}_2\text{NHSiMe}_3$  (Kel-F/Nujol mull).

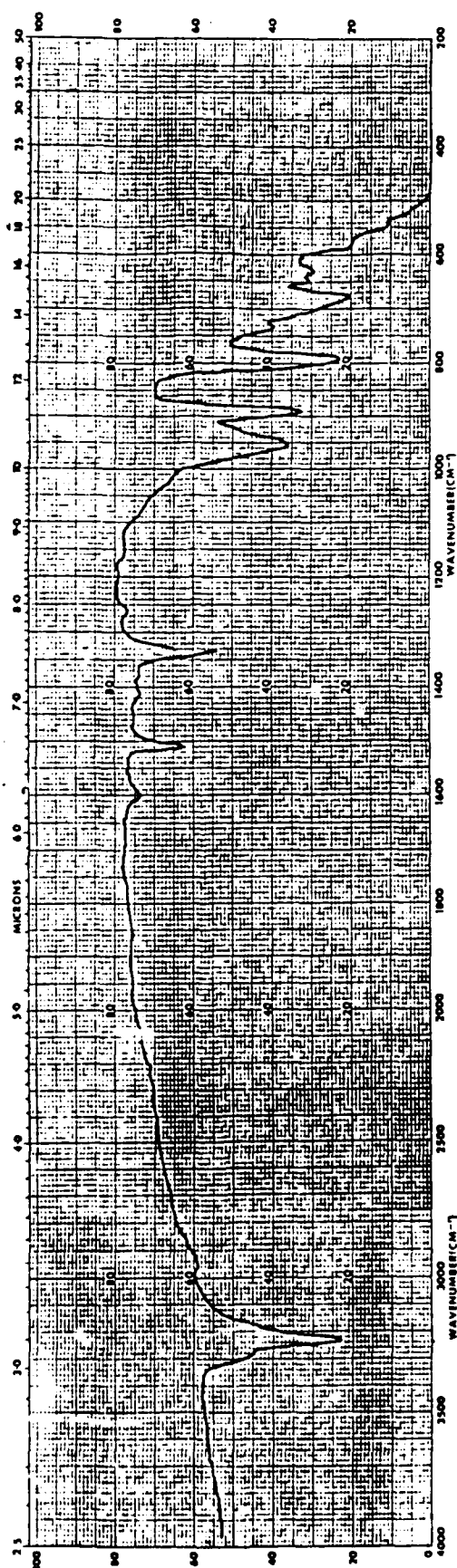


Figure A-6: Infrared spectrum of  $[\text{AlClNH}]_4$  (Kel-F/Nujol mull).



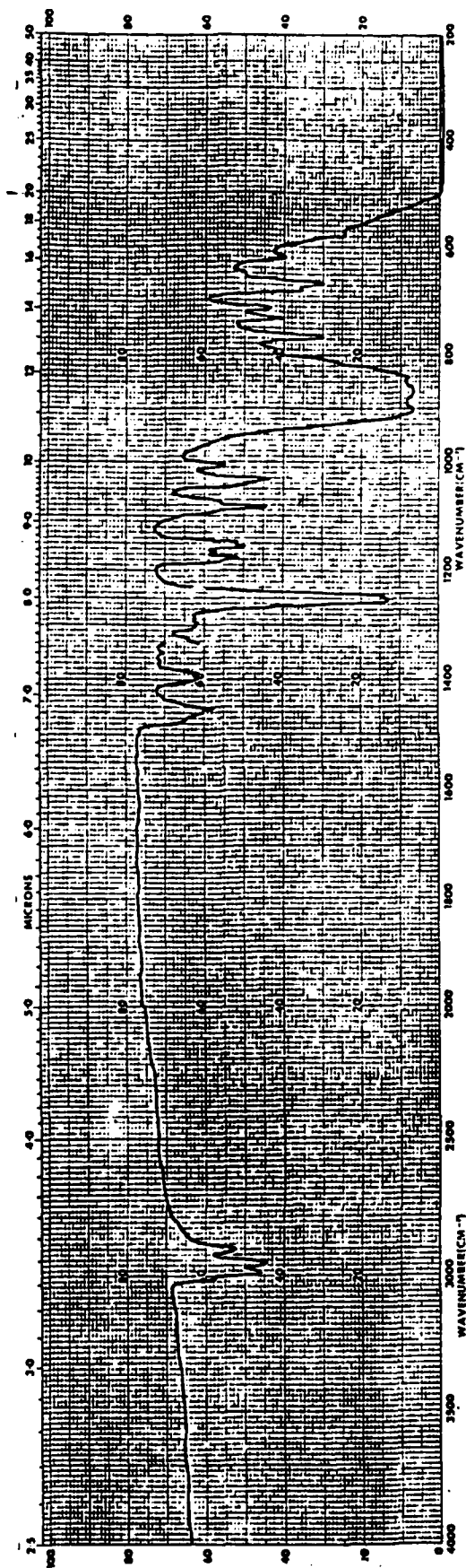


Figure A-7: Infrared spectrum of  $\text{AlCl}_2\text{N}(\text{SiMe}_3)_2 \cdot \text{NEt}_3$  (Kel-F/Nujol mull).

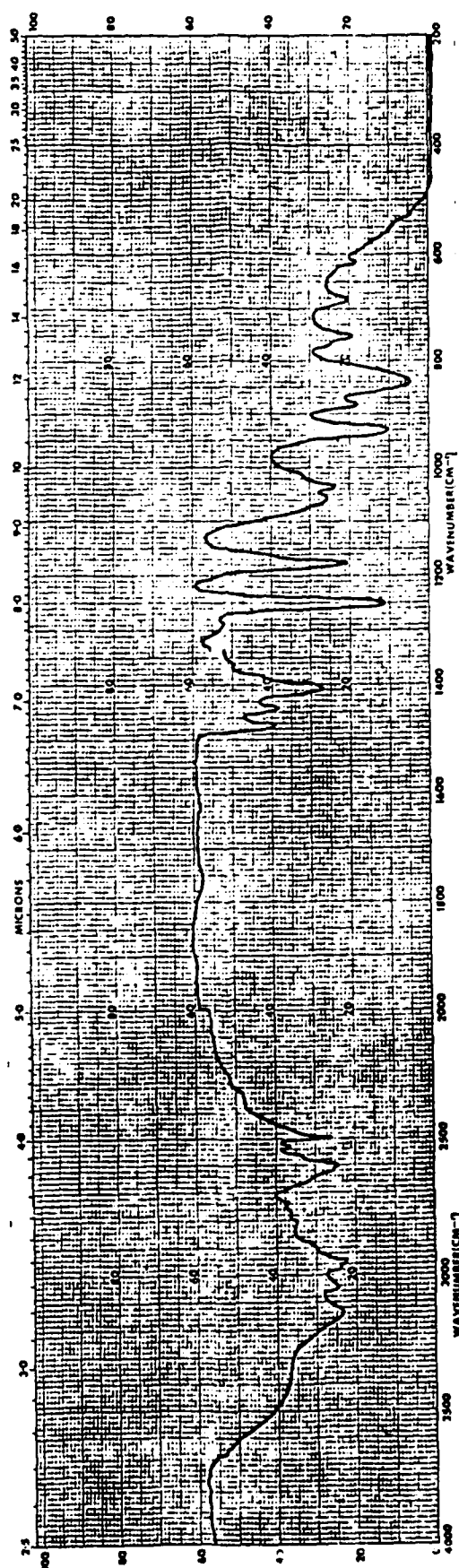


Figure A-8: Infrared spectrum of  $\text{AlCl}_2\text{N}(\text{SiMe}_3)_2 \cdot \text{NEt}_3$  following exposure to atmosphere (Kel-F/Nujol mull).

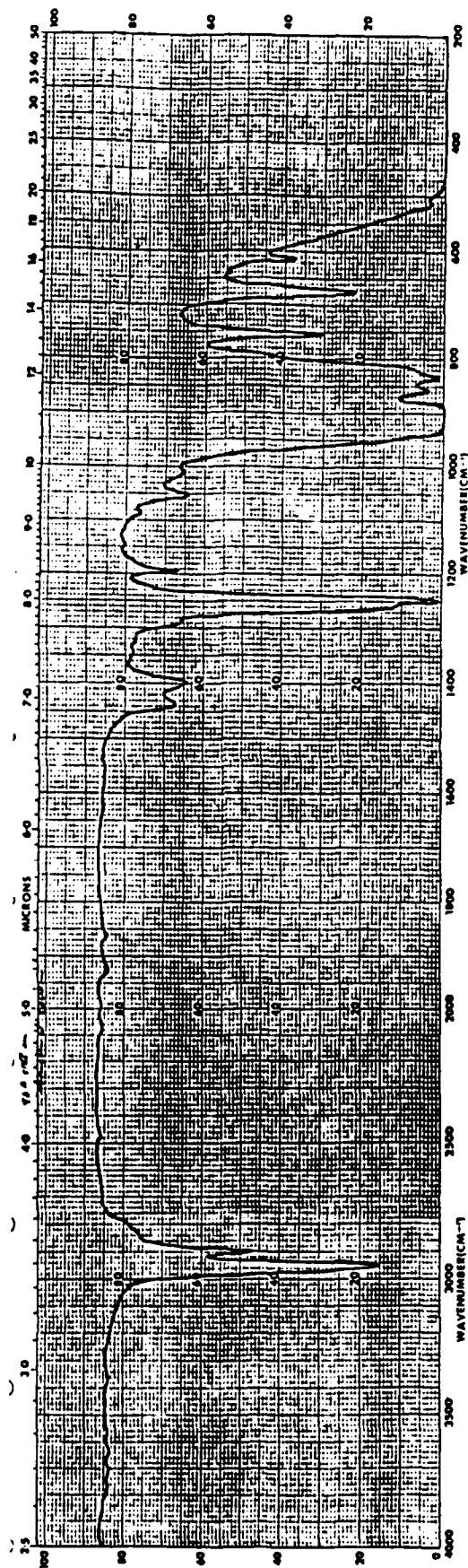


Figure A-9: Infrared spectrum of  $\text{AlCl}[\text{N}(\text{SiMe}_3)_2]_2$  (neat).

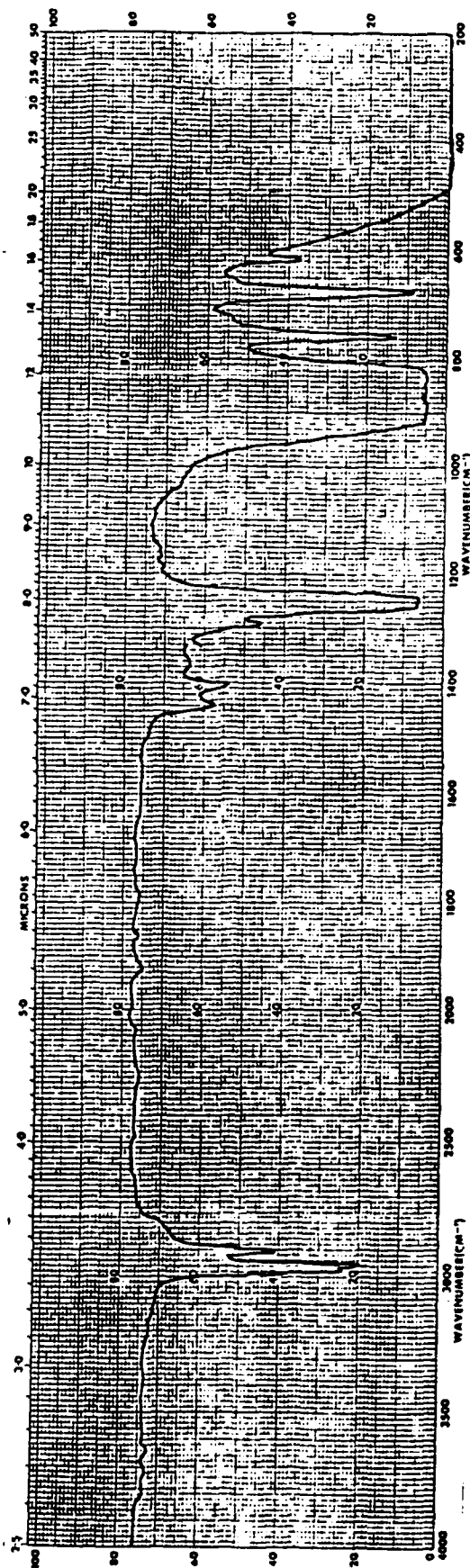


Figure A-10: Infrared spectrum of  $\text{Al}[\text{N}(\text{SiMe}_3)_2]_3$  (Kel-F/Nujol mull).

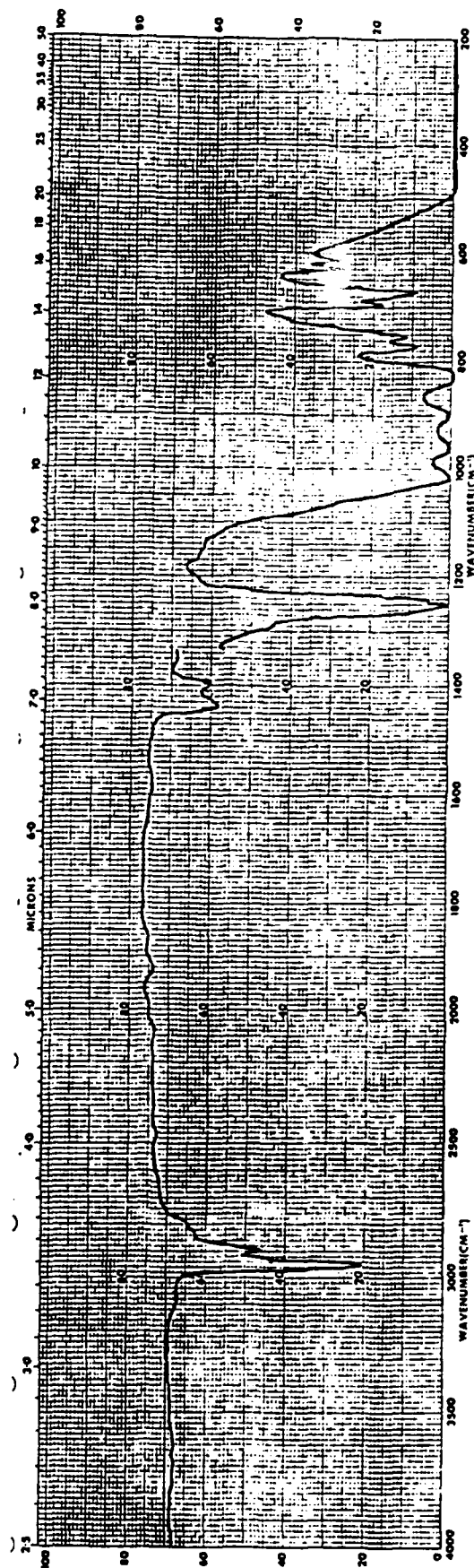


Figure A-11: Infrared spectrum of  $[\text{Me}_3\text{SiAlN}(\text{SiMe}_3)_2]_2$  (Kel-F/Nujol mull).

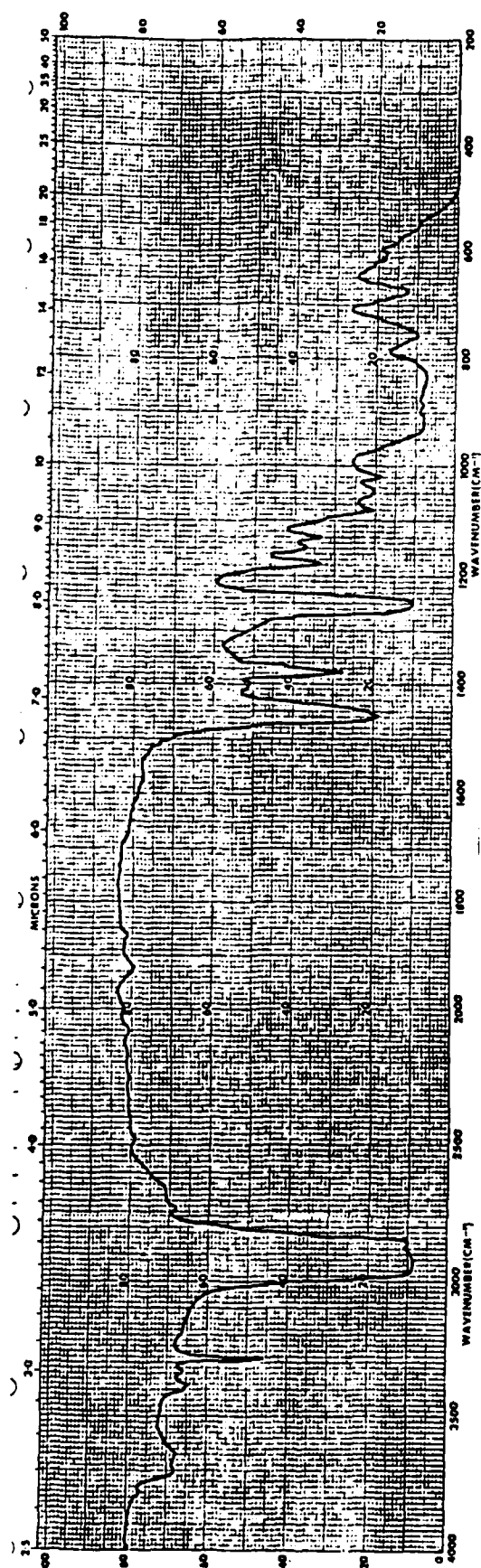


Figure A-12: Infrared spectrum of  $[\text{Me}_3\text{SiAlN}(\text{SiMe}_3)_2]_2$  following exposure to atmosphere (Nujol mull).

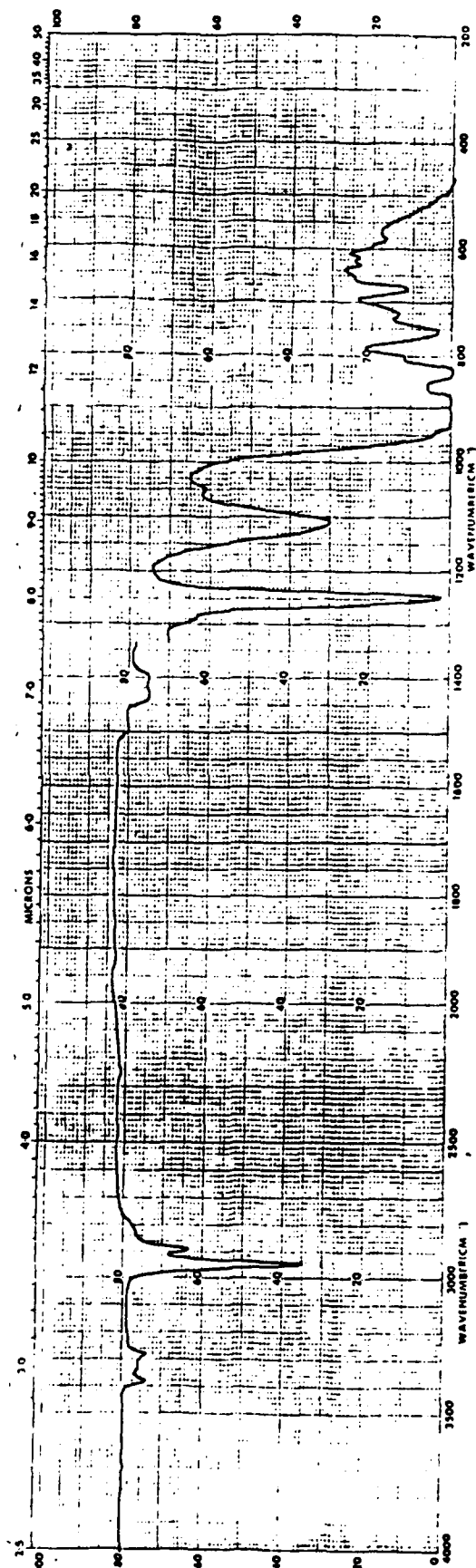


Figure A-13: Infrared spectrum of  $\text{Me}_3\text{SiAl}(\text{NH}_2)\text{N}(\text{SiMe}_3)\text{AlNH}_2\text{SiMe}_3$  (Kel-F/Nujol mull).

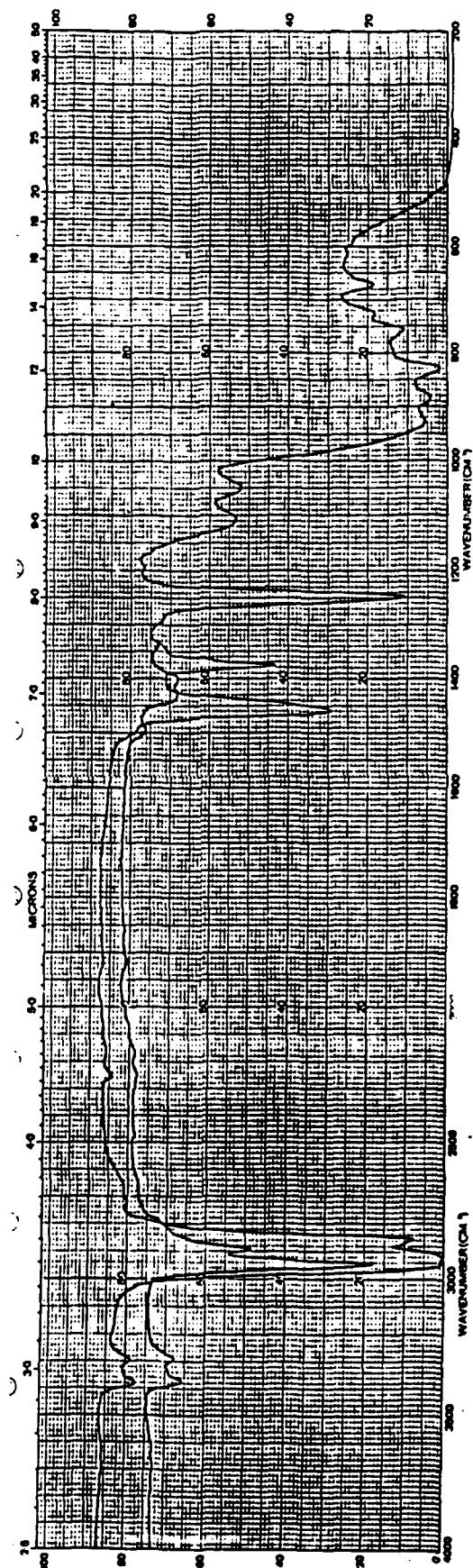


Figure A-14: Infrared spectrum of the pyrolysis product of  $\text{Me}_3\text{SiAl}(\text{NH}_2)\text{NSiMe}_3\text{AlNHSiMe}_3$  (Kel-F/Nujol mull).



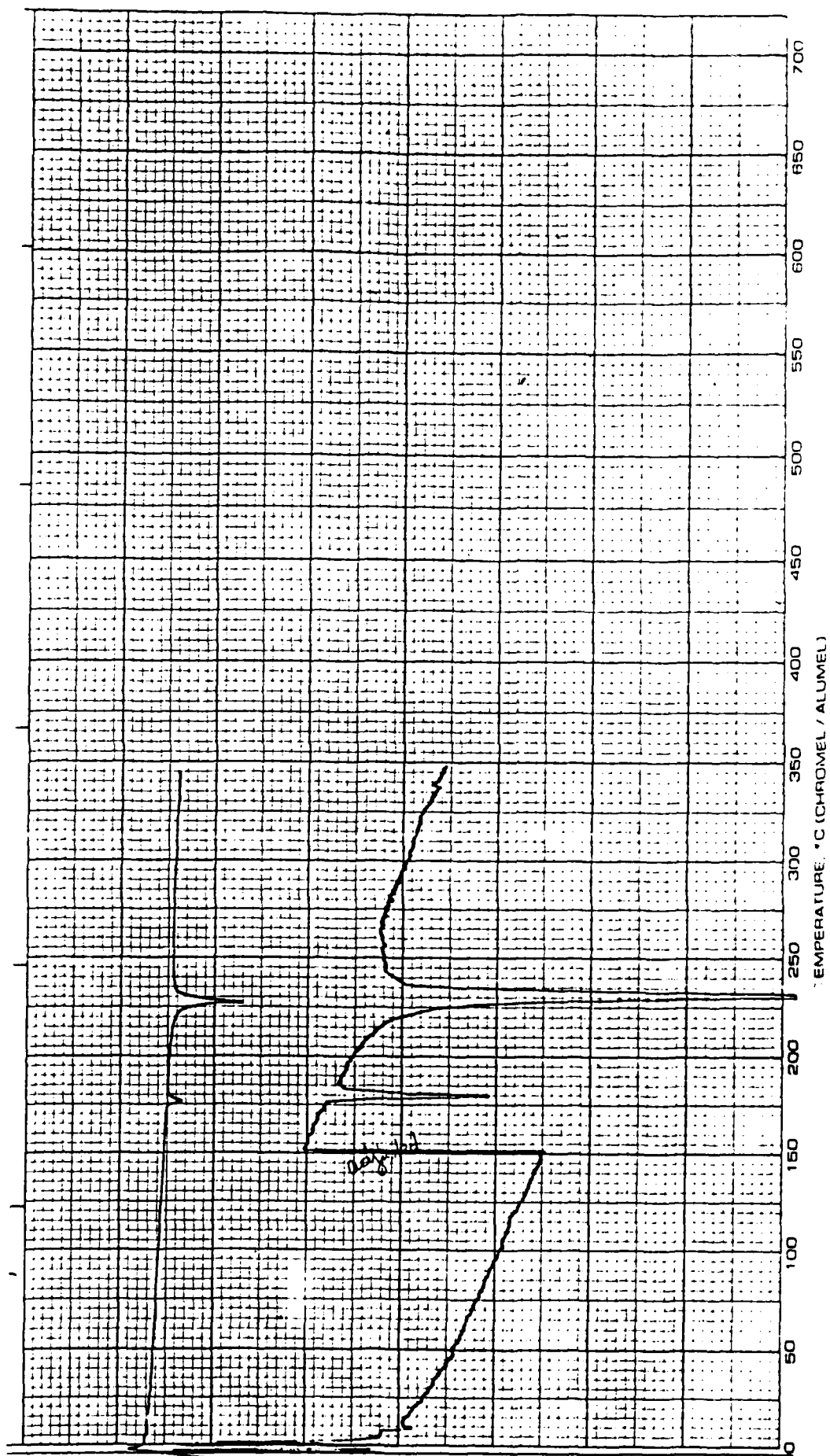


Figure A-15: DSC scan of  $[[(\text{Me}_3\text{Si})_2\text{N}]_2\text{AlNH}_2]_2$ .

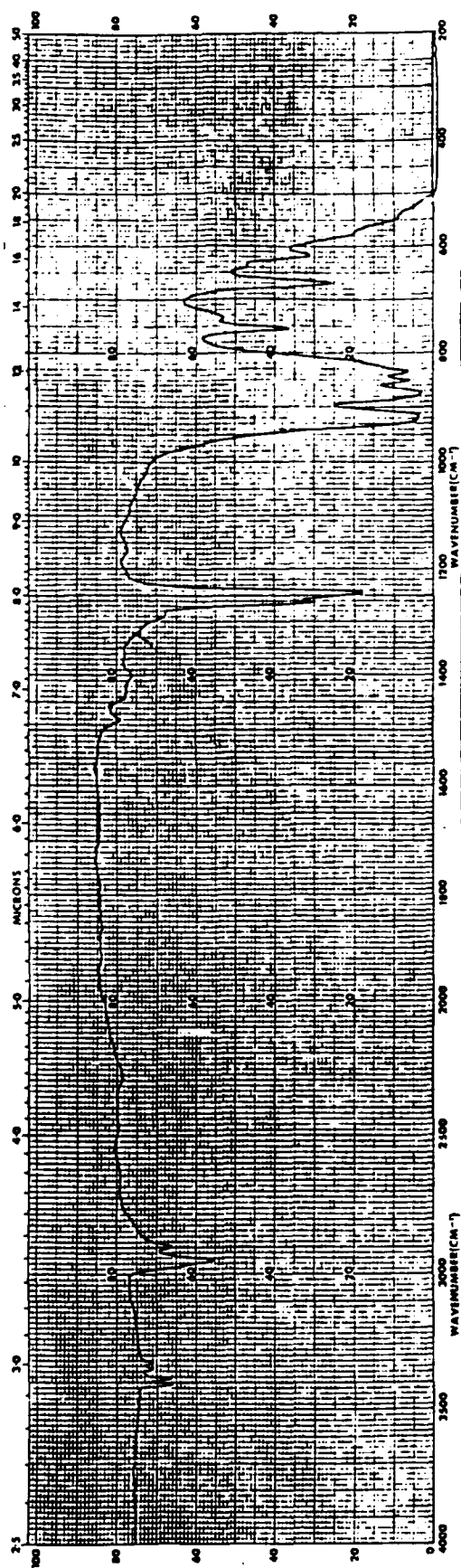


Figure A-16: Infrared spectrum of  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{AlNH}_2]_2$  (Kel-F/Nujol mull).

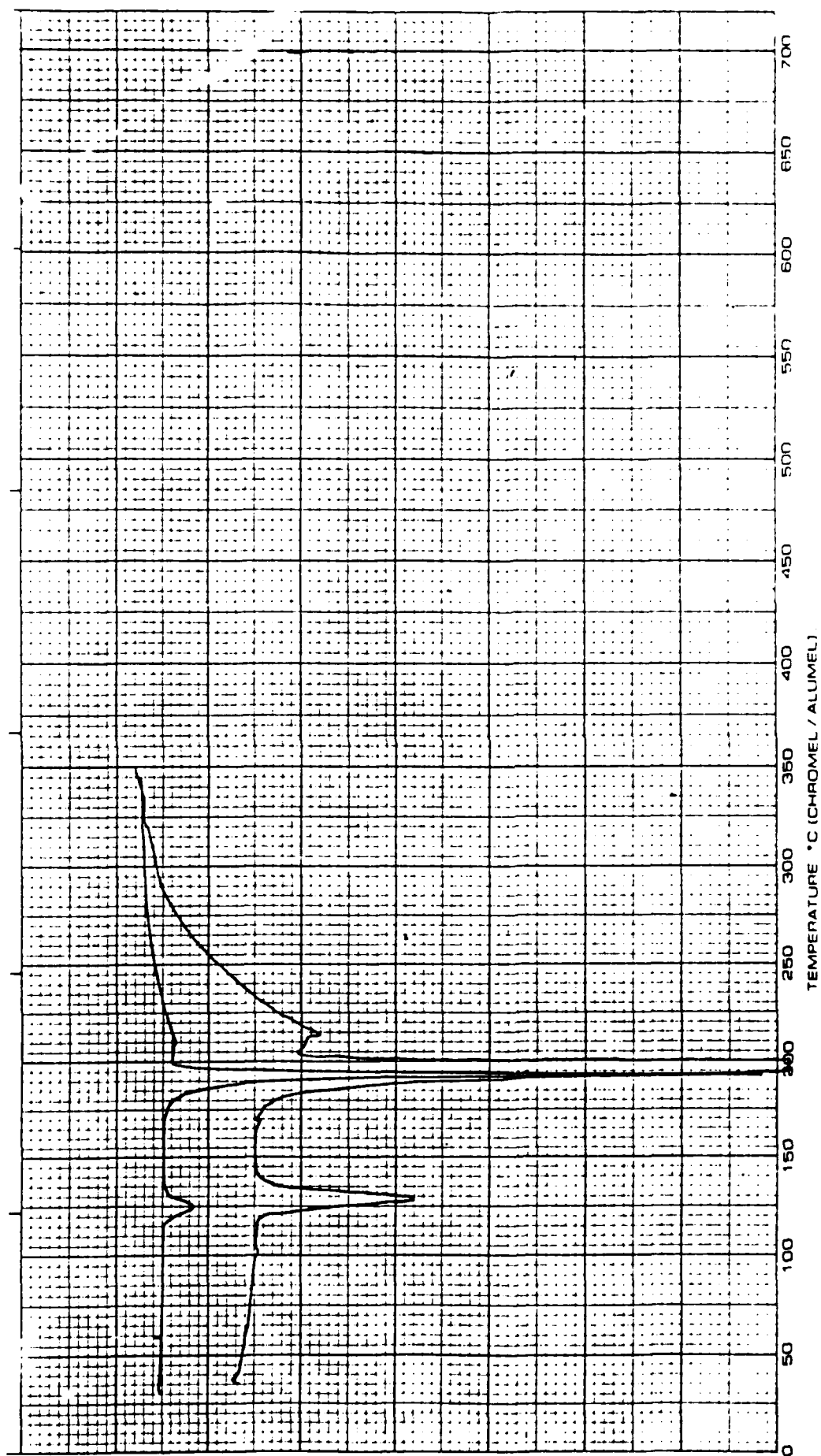


Figure A-17: DSC scan of  $[[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\text{NH}_2)_2]_3\text{Al}$ .

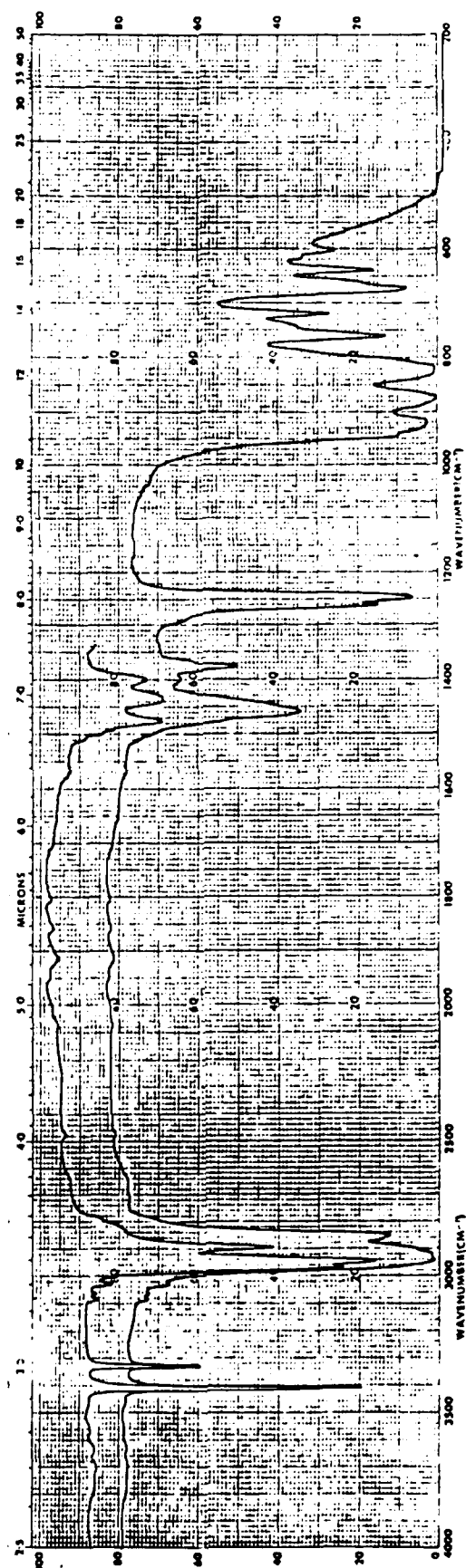


Figure A-18: Infrared spectrum of  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\text{NH}_2)_2]_3\text{Al}$  (Kel-F/Nujol mull).

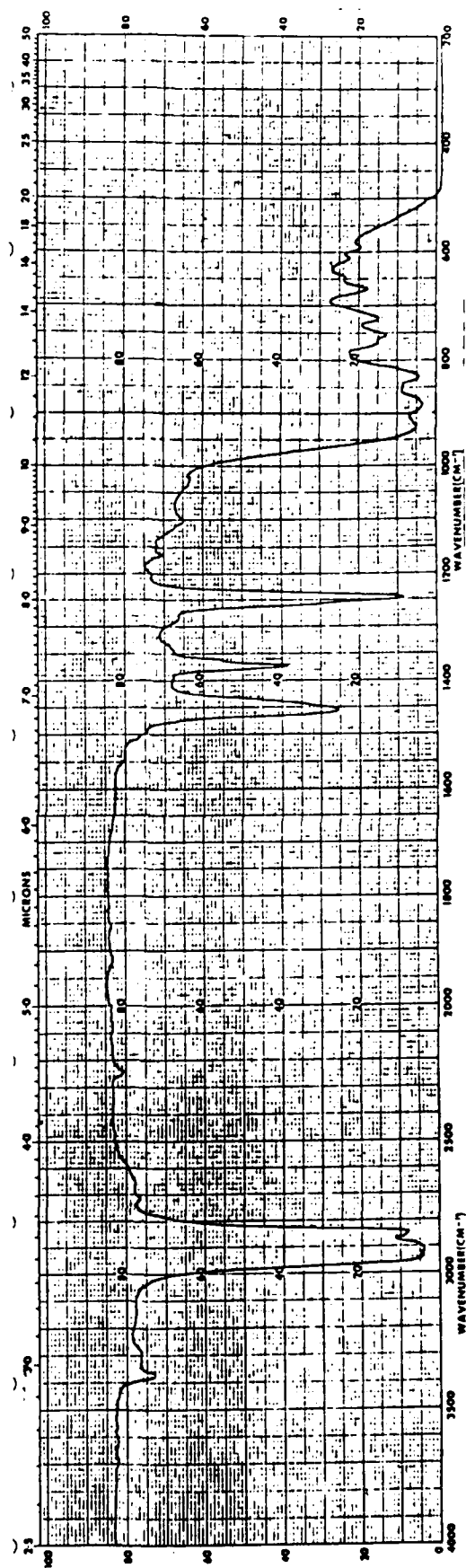


Figure A-19: Infrared spectrum of  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{AlNH}_2]_2$  pyrolysis residue (Kel-F/Nujol mull).

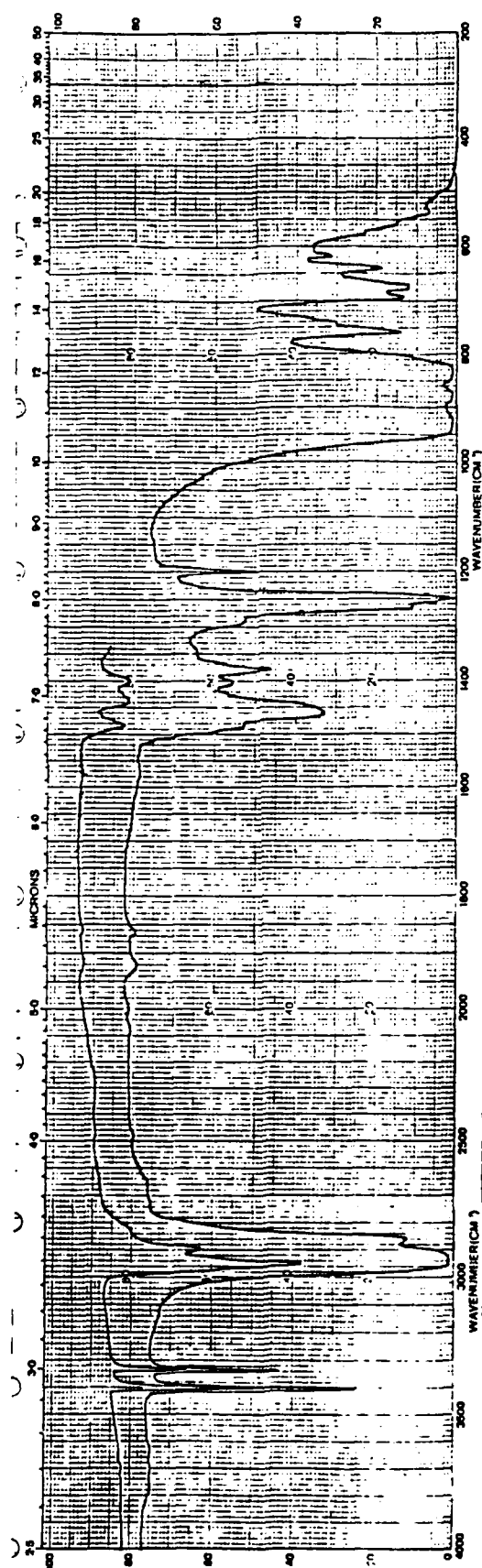


Figure A-20: Infrared spectrum of the reaction product of  $\text{AlCl}[\text{N}(\text{SiMe}_3)_2]_2$  with ammonia at  $-20^\circ\text{C}$ .

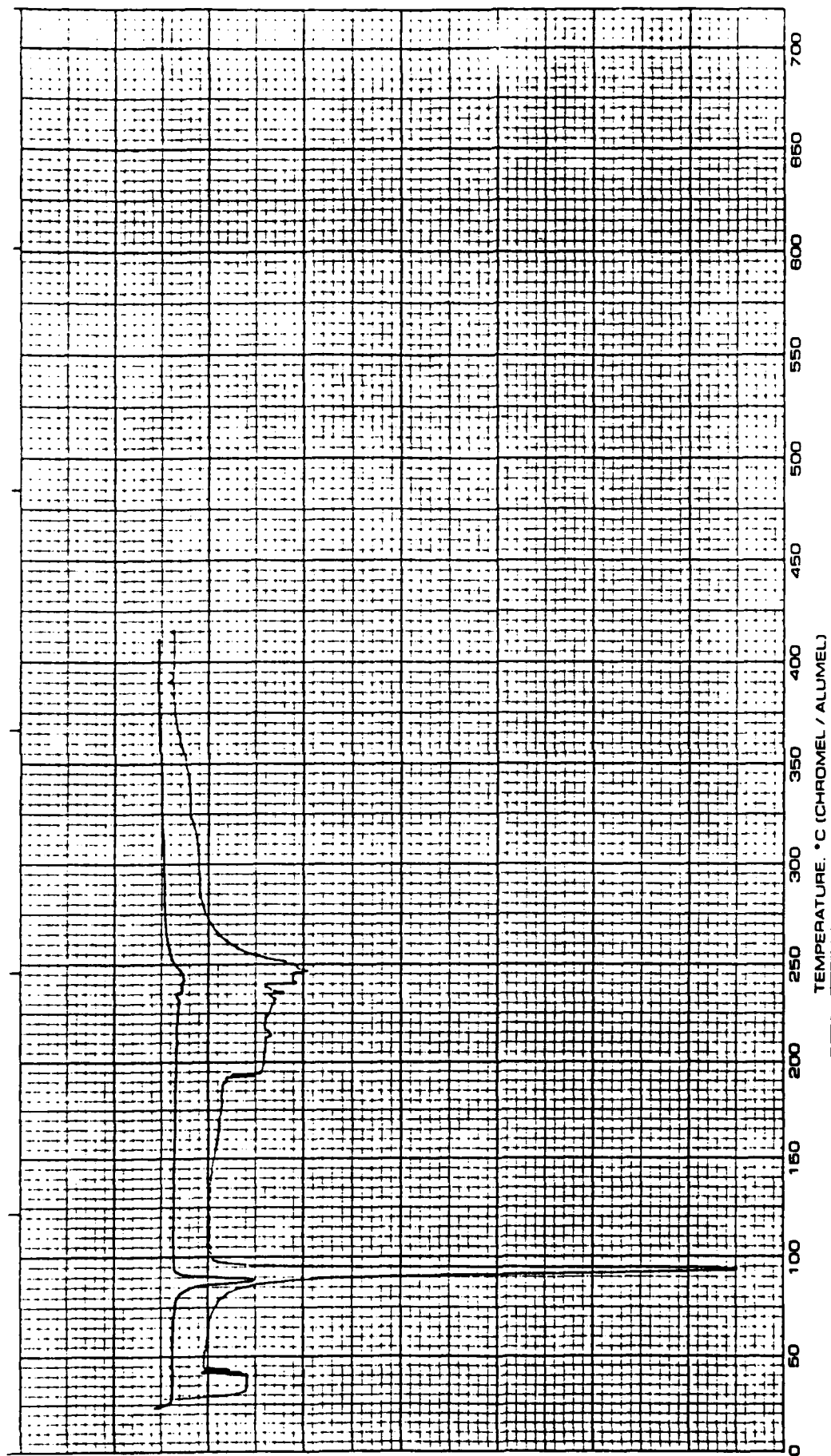


Figure A-21: DSC scan of the reaction product of  $\text{AlCl}[\text{N}(\text{SiMe}_3)_2]_2$  with ammonia at  $-20^\circ\text{C}$ .

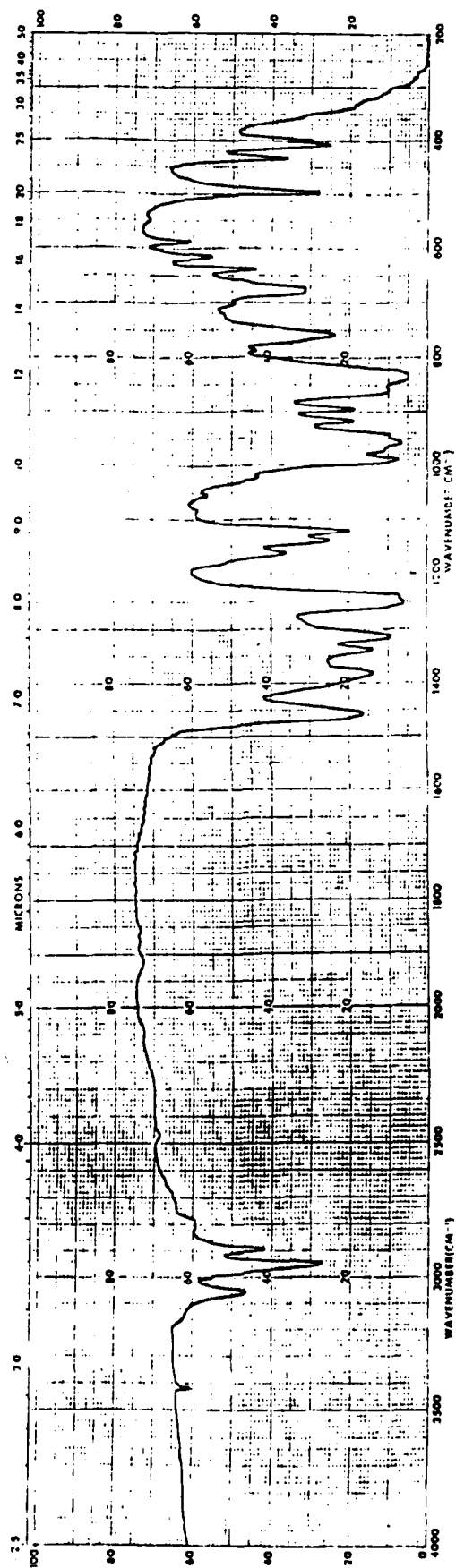


Figure A-22: Infrared spectrum of  $\text{Et}_3\text{N} \cdot \text{Cl}_2\text{AlN}(\text{SiMe}_3)\text{B}(\text{NH}_2)\text{NHSiMe}_3$  (Kel-F/Nujol mull).



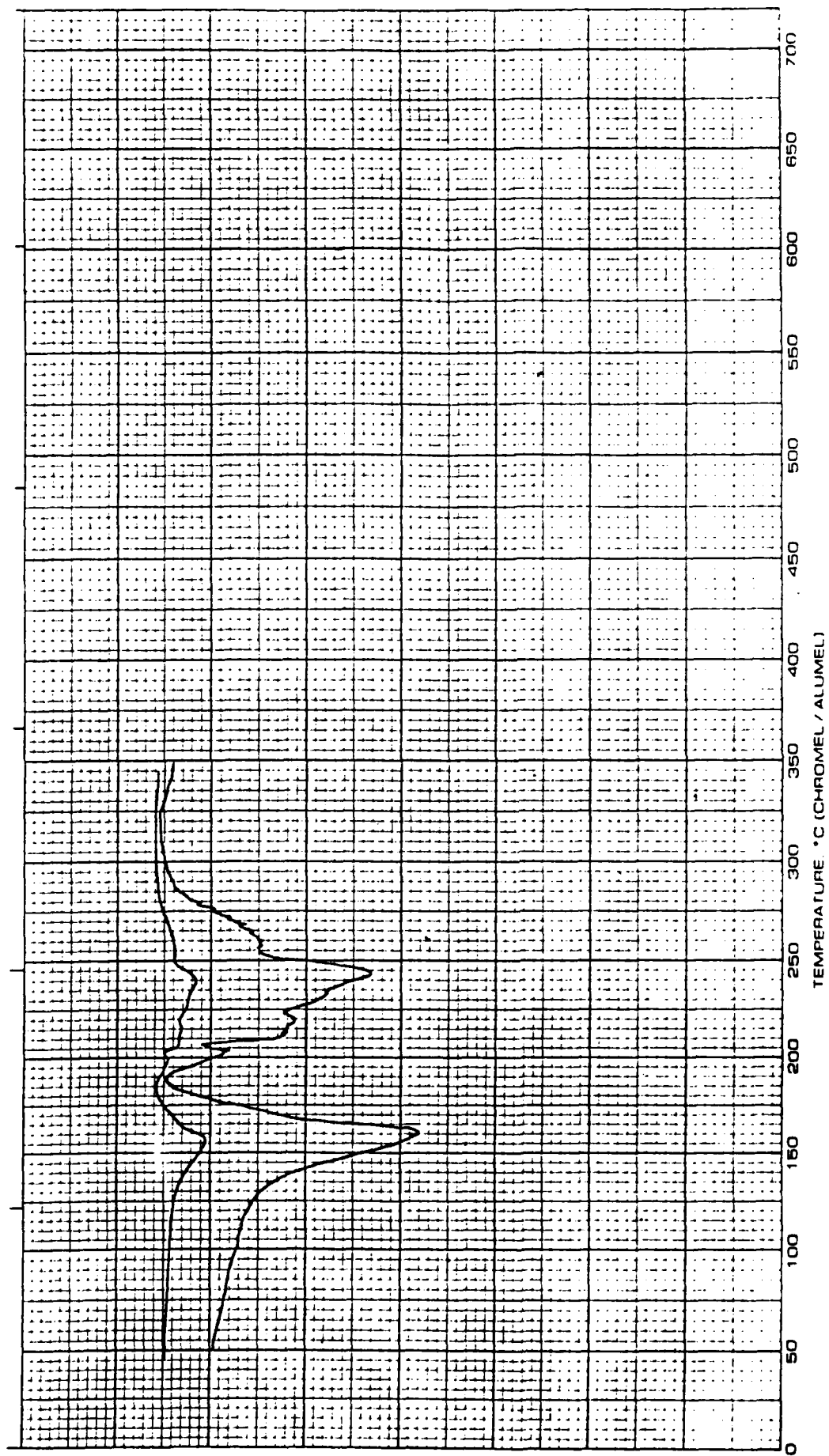


Figure A-23: DSC scan of  $\text{Et}_3\text{N} \cdot \text{Cl}_2\text{AlN}(\text{SiMe}_3)\text{B}(\text{NH}_2)\text{NHSiMe}_3$ .

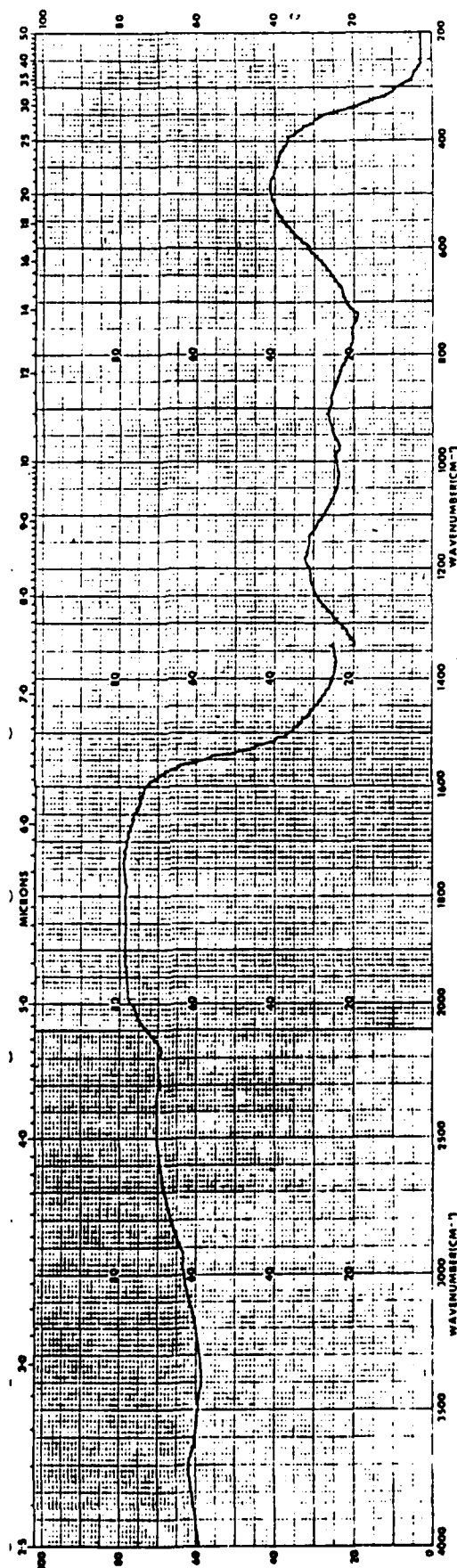


Figure A-24: Infrared spectrum of the TGA residue from  $\text{Et}_3\text{N} \cdot \text{Cl}_2\text{AlN}(\text{SiMe}_3)_3$  (10°C/min, room temperature to 1000°C).

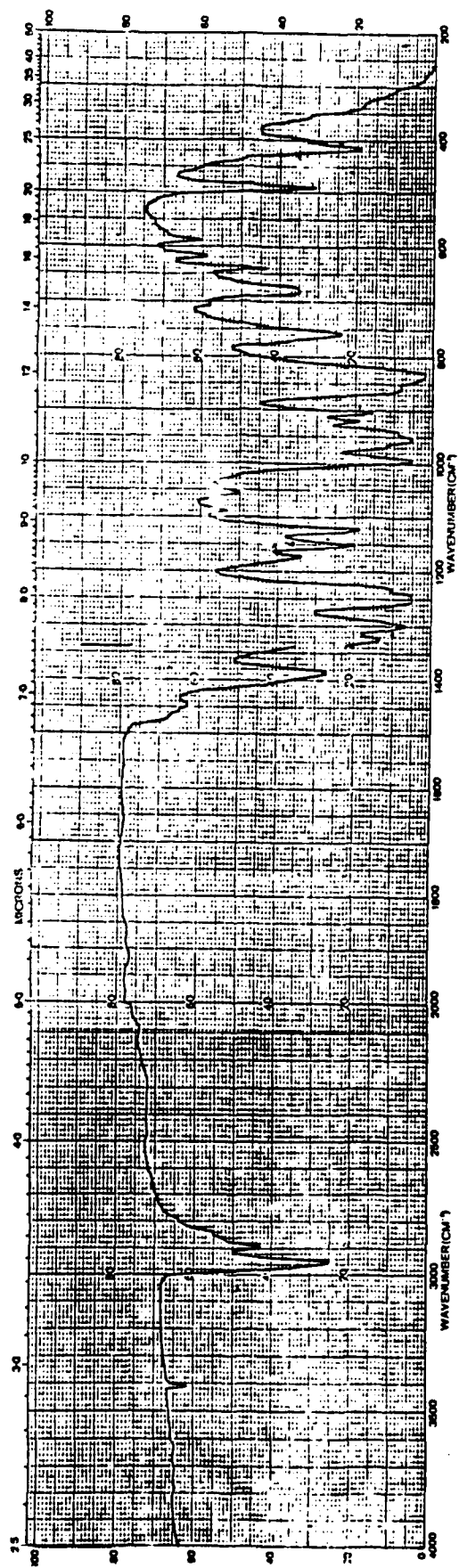


Figure A-25: Infrared spectrum of the reaction product of  $\text{Et}_3\text{N} \cdot \text{AlCl}_2\text{N}(\text{SiMe}_3)\text{B}(\text{NH}_2)\text{NHSiMe}_3$  with 1 equivalent of  $\text{LiN}(\text{SiMe}_3)_2$ .

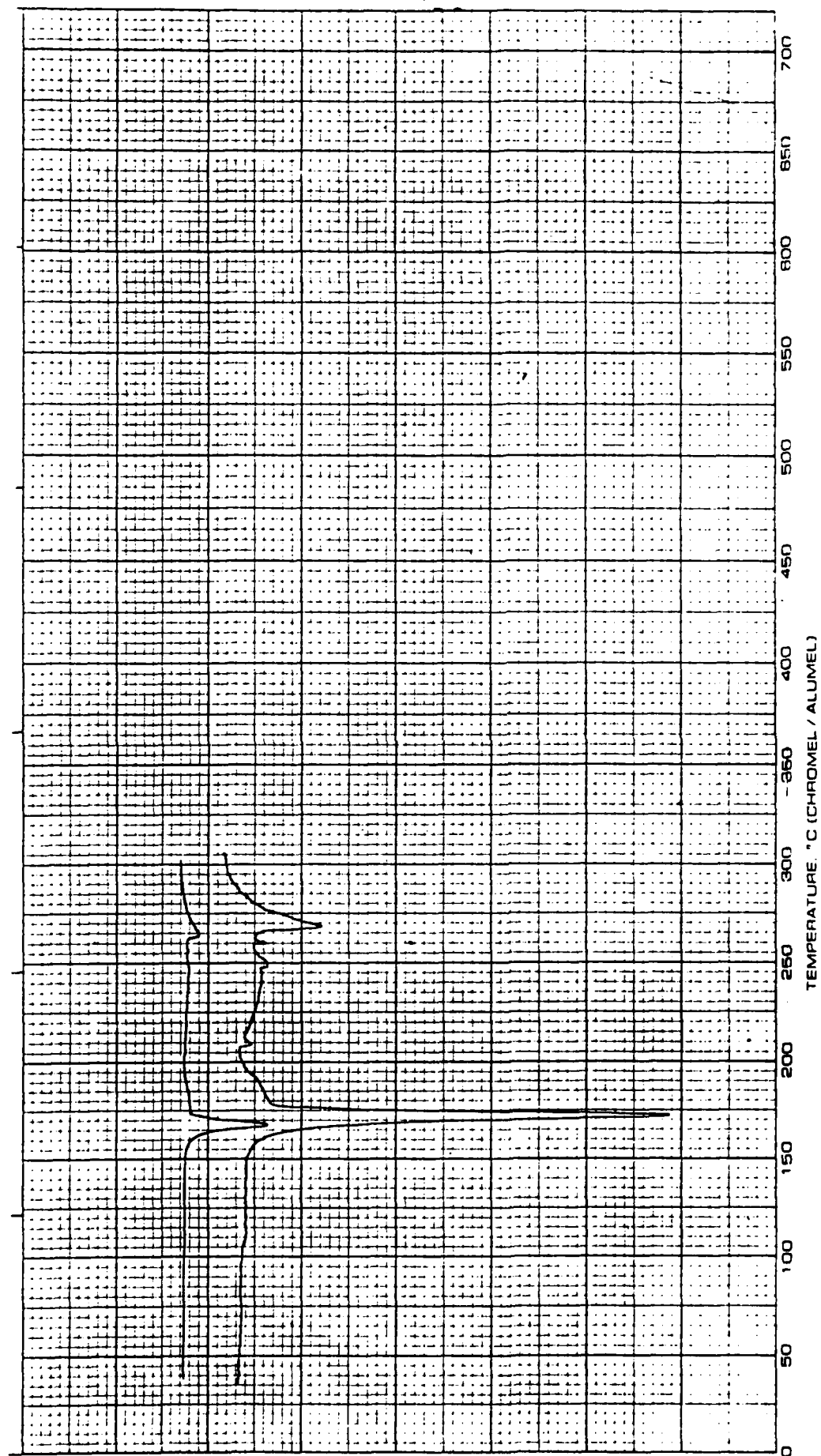


Figure A-26: DSC scan of the reaction product of  $\text{Et}_3\text{N} \cdot \text{Cl}_2\text{AlN}(\text{SiMe}_3)\text{B}(\text{NH}_2)\text{NHSiMe}_3$  with 1 equivalent of  $\text{LiN}(\text{SiMe}_3)_2$ .

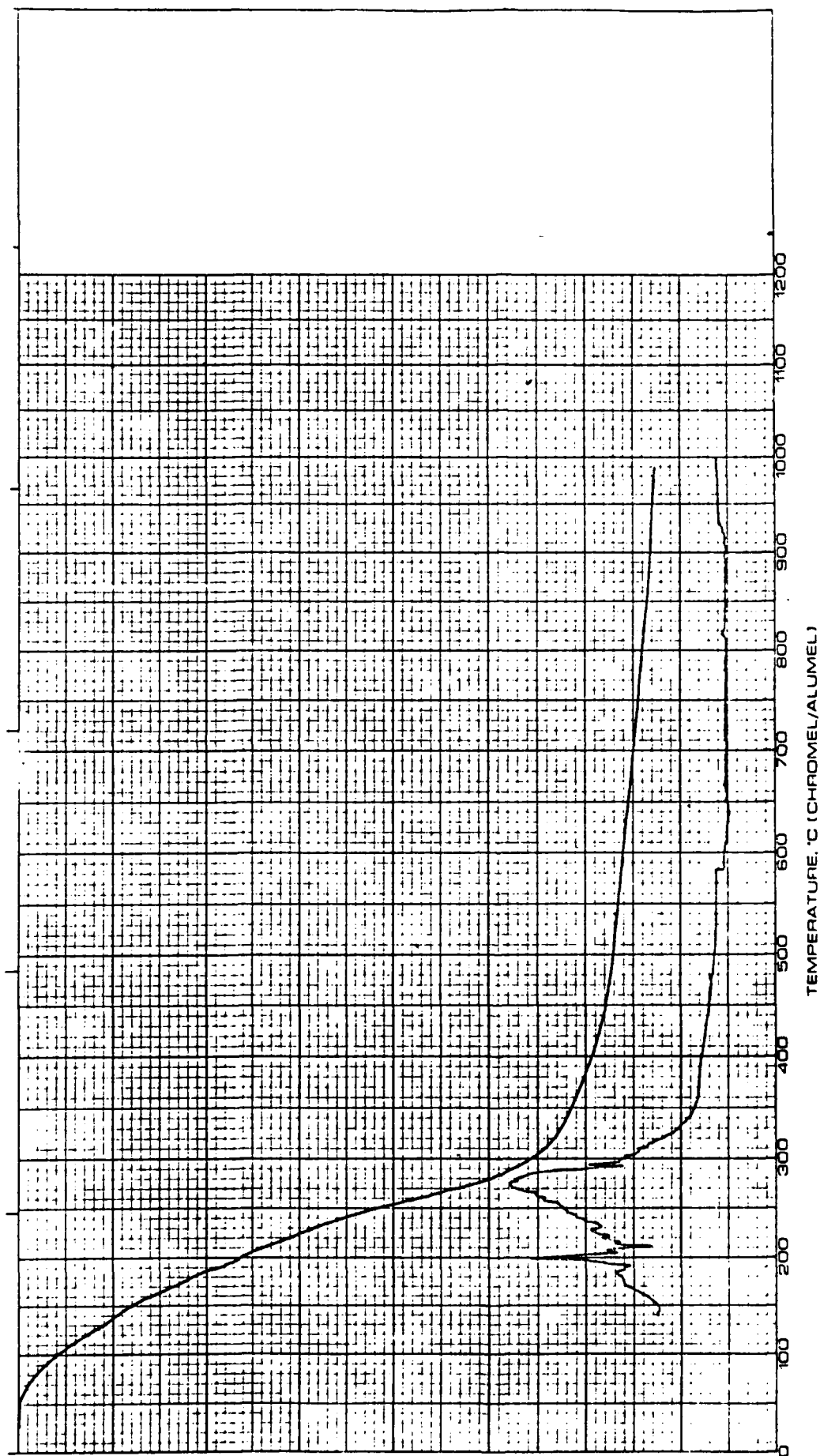


Figure A-27: TGA scan of the reaction product of  $\text{Et}_3\text{N} \cdot \text{Cl}_2\text{AlN}(\text{SiMe}_3)\text{B}(\text{NH}_2)\text{NHSiMe}_3$  with 1 equivalent of  $\text{LiN}(\text{SiMe}_3)_2$ .

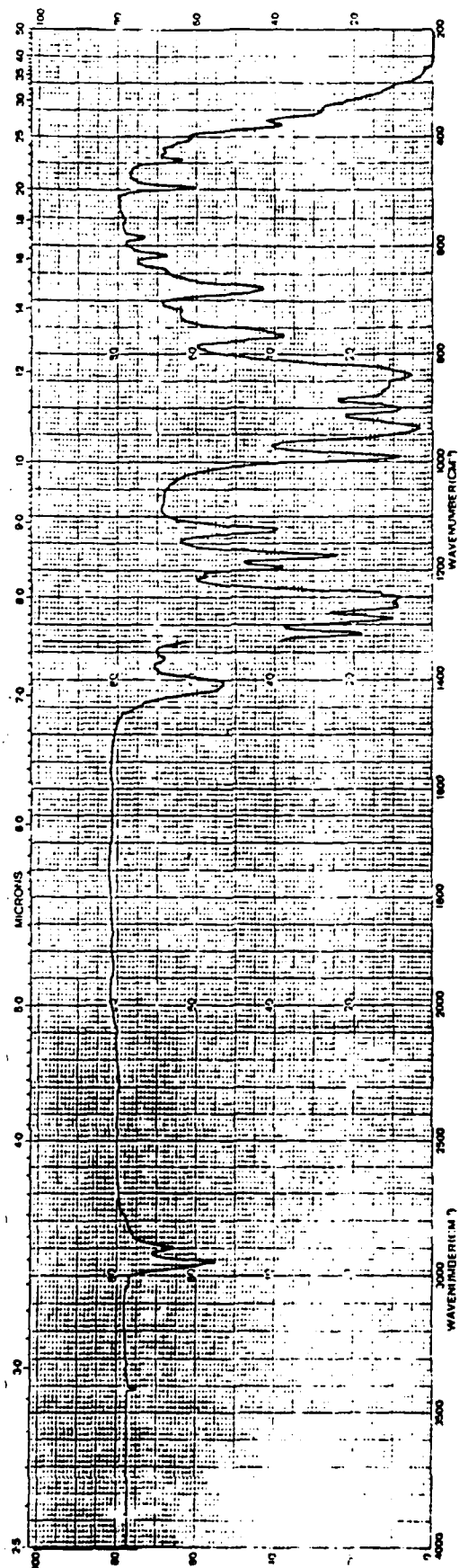


Figure A-28: Infrared spectrum of the reaction product of  $\text{Et}_3\text{N} \cdot \text{Cl}_2\text{AlN}(\text{SiMe}_3)\text{B}(\text{NH}_2)\text{NHSiMe}_3$  with 2 equivalents of  $\text{LiN}(\text{SiMe}_3)_2$ .

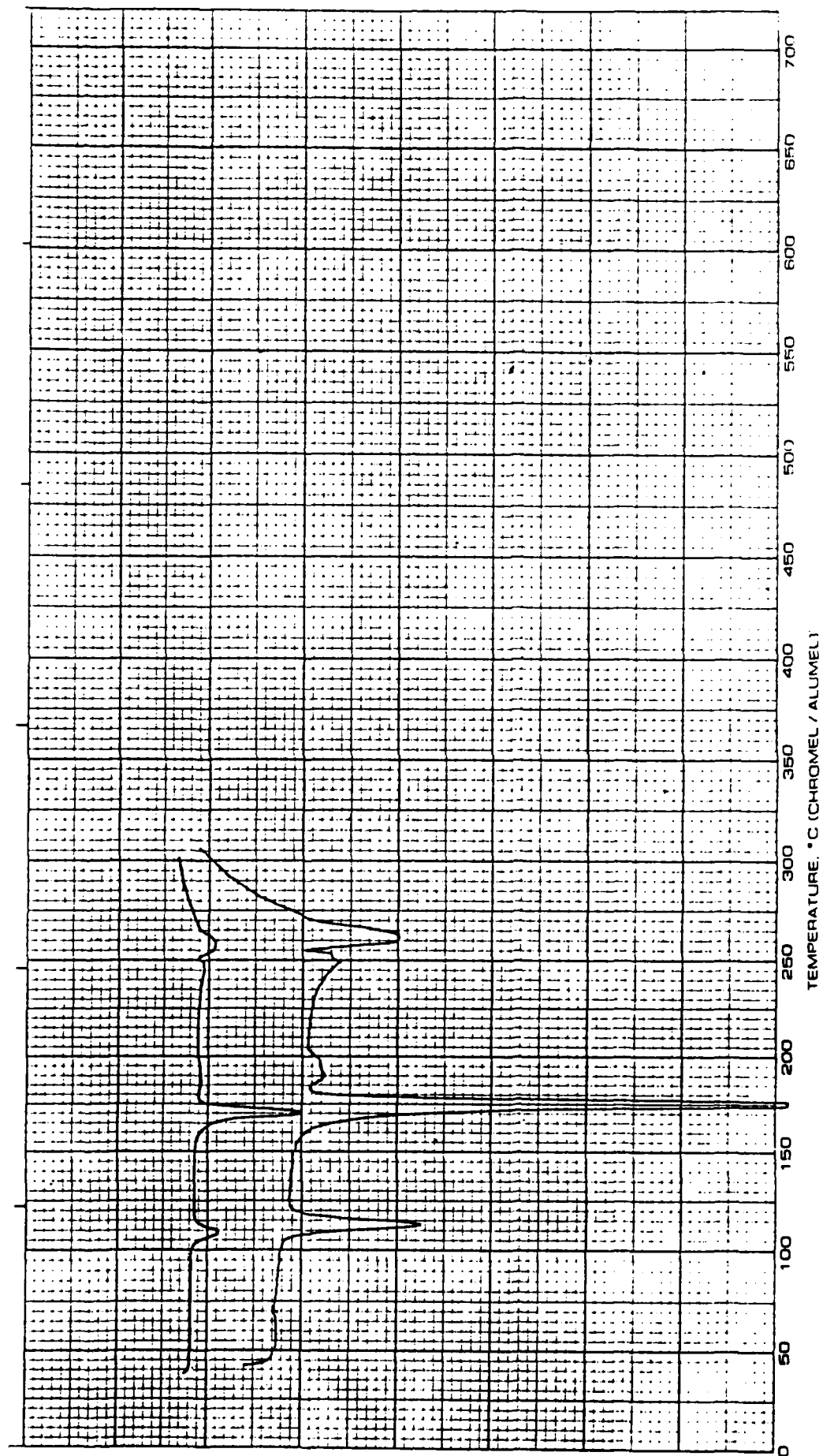


Figure A-29: DSC scan of the reaction product of  $\text{Et}_3\text{N} \cdot \text{Cl}_2\text{AlN}(\text{SiMe}_3)\text{B}(\text{NH}_2)\text{NHSiMe}_3$  with 2 equivalents of  $\text{LiN}(\text{SiMe}_3)_2$ .

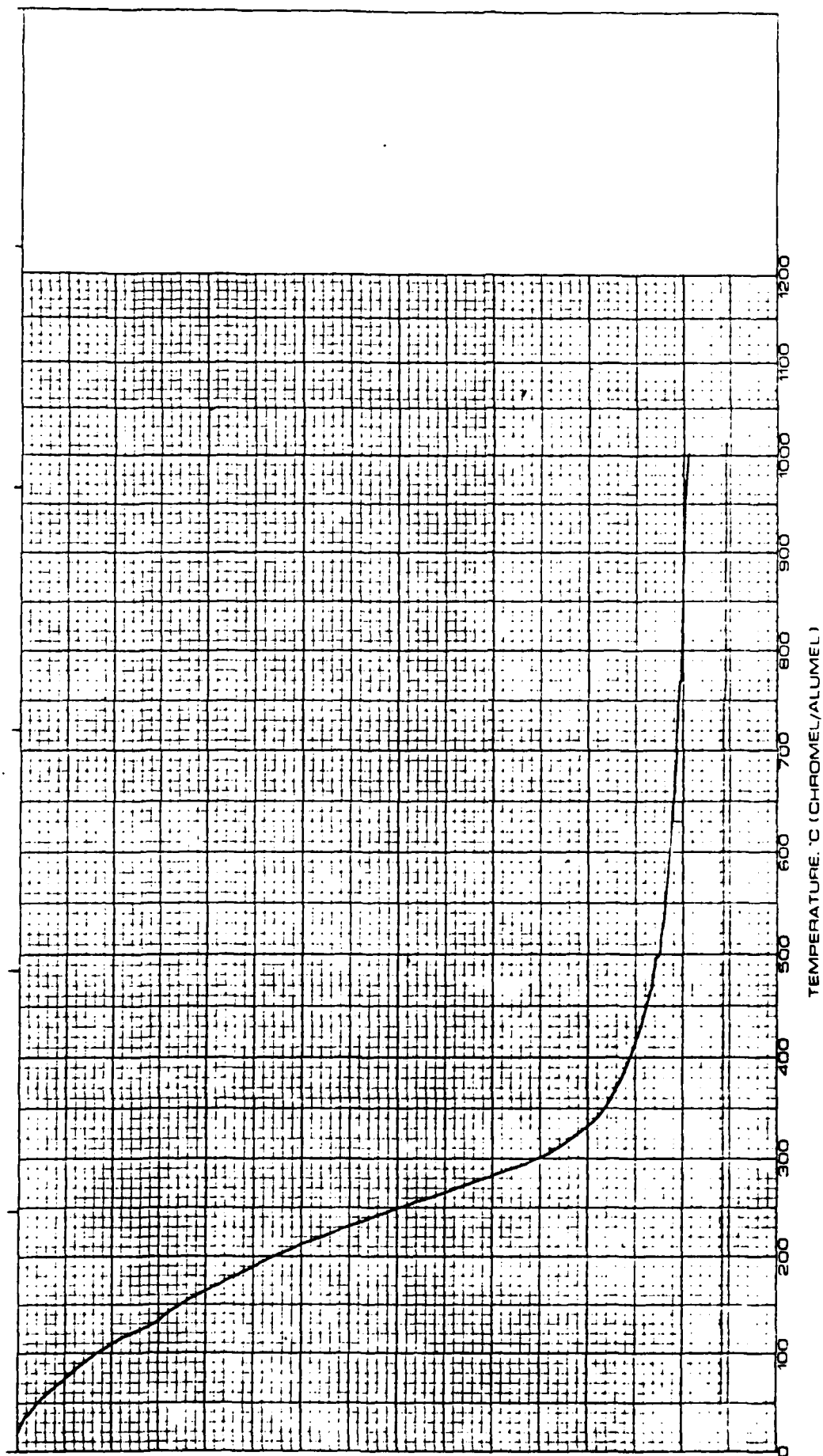


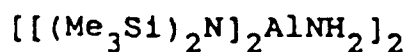
Figure A-30: TGA scan of the reaction product of  $\text{Et}_3\text{N} \cdot \text{Cl}_2\text{AlN}(\text{SiMe}_3)\text{B}(\text{NH}_2)\text{NHSiMe}_3$  with 2 equivalents of  $\text{LiN}(\text{SiMe}_3)_2$ .



Table A-1. Summary of Crystallographic Data for  
 $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\text{NH}_2)_2$  and  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\text{NH}_2)_2\text{Al}_3$

chem. formula:	$\text{C}_{24}\text{H}_{76}\text{N}_6\text{Al}_2\text{Si}_8$	$\text{C}_{36}\text{H}_{120}\text{N}_{12}\text{Al}_4\text{Si}_{12} \cdot 1/2(\text{C}_6\text{H}_{14})$
fw:	727.6	1209.5
Space group:	$\text{P}2_1/\text{c}$	$\text{C}2/\text{c}$
Temp, °K:	295	295
$\lambda$ , Å:	1.54178	1.54178
$\rho$ (calcd), $\text{g}/\text{cm}^3$ :	1.054	1.045
$\mu$ , $\text{cm}^{-1}$ :	27.8	26.5
$a$ , Å:	9.162 (2)	25.993 (3)
$b$ , Å:	14.580 (3)	15.092 (2)
$c$ , Å:	34.444 (5)	41.084 (5)
$\beta$ , deg:	94.94 (1)	107.49 (1)
$v$ , Å <sup>3</sup> :	4584 (2)	15373 (4)
$Z$ :	4	8
$R(F)$ :	0.0634	0.0774
$R_w(F)$ :	0.0573	0.0699
Transmission coeff:	0.49-0.80	0.6813-0.8420

Table A-2: Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Coefficients ( $\text{\AA}^2 \times 10^3$ ) for



	x	y	z	U(eq)
Al(1)	2178(2)	3470(1)	1495(1)	42(1)
Al(2)	3061(2)	2038(1)	993(1)	39(1)
Si(1)	4317(2)	3067(1)	260(1)	58(1)
Si(2)	2136(2)	1574(1)	154(1)	54(1)
Si(3)	5291(2)	546(1)	1218(1)	53(1)
Si(4)	2226(2)	50(1)	1327(1)	57(1)
Si(5)	2912(2)	2782(1)	2369(1)	58(1)
Si(6)	-99(2)	3346(1)	2089(1)	61(1)
Si(7)	3192(2)	5473(1)	1576(1)	79(1)
Si(8)	803(2)	5101(1)	958(1)	70(1)
N(1)	3994(5)	2909(4)	1361(2)	45(2)
N(2)	1265(5)	2559(3)	1149(2)	44(2)
N(3)	3172(4)	2296(3)	470(1)	42(1)
N(4)	3446(4)	876(3)	1181(1)	41(1)
N(5)	1719(4)	3184(3)	1989(1)	44(1)
N(6)	2055(5)	4669(3)	1323(1)	52(2)
C(1)	5506(8)	3752(4)	618(2)	92(3)
C(2)	3278(8)	3967(4)	-38(2)	90(3)
C(3)	5577(7)	2482(5)	-68(2)	91(3)
C(4)	314(6)	1323(4)	344(2)	72(2)
C(5)	1662(8)	2062(5)	-343(2)	95(3)
C(6)	3091(7)	464(4)	89(2)	78(3)
C(7)	6193(7)	720(5)	1723(2)	75(3)
C(8)	6366(6)	1255(5)	892(2)	76(3)
C(9)	5610(8)	-672(4)	1066(2)	83(3)
C(10)	477(6)	551(4)	1483(2)	82(3)
C(11)	1680(9)	-813(4)	940(2)	94(3)
C(12)	2967(7)	-636(4)	1762(2)	74(3)
C(13)	4870(7)	3071(7)	2322(2)	113(4)
C(14)	2879(10)	1521(4)	2398(2)	122(4)
C(15)	2561(9)	3269(6)	2853(2)	103(3)
C(16)	-782(8)	2411(6)	2406(2)	109(4)
C(17)	-427(9)	4474(5)	2314(2)	121(4)
C(18)	-1395(6)	3307(5)	1635(2)	80(3)
C(22)	-724(9)	5746(6)	1165(2)	122(4)
C(23)	1672(9)	5878(5)	613(2)	102(3)
C(24)	-115(7)	4211(4)	634(2)	87(3)
C(19)	2941(25)	5454(18)	2107(5)	118(9)
C(20)	5220(16)	5177(16)	1563(8)	97(8)
C(21)	3126(38)	6679(16)	1452(11)	160(16)
C(19A)	4785(29)	5743(24)	1278(12)	146(15)
C(20A)	3736(58)	5220(27)	2073(10)	312(30)
C(21A)	2171(38)	6603(22)	1589(10)	124(14)

\* Equivalent isotropic U defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor

Table A-3: Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Coefficients ( $\text{\AA}^2 \times 10^3$ ) for  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\text{NH}_2)]_3\text{Al}$

	x	y	z	U(eq)
C(1)	-20(5)	12913(5)	945(3)	119(6)
C(2)	-961(3)	11653(8)	742(2)	107(5)
C(3)	33(3)	11250(6)	566(2)	79(4)
C(4)	-950(3)	10636(7)	1492(3)	103(5)
C(5)	-556(4)	12519(6)	1615(3)	121(6)
C(6)	55(3)	11059(7)	2041(2)	99(5)
C(7)	1568(4)	11261(8)	2531(2)	131(6)
C(8)	2262(3)	10020(8)	2259(3)	111(5)
C(9)	1254(4)	9432(7)	2324(2)	108(5)
C(10)	1111(4)	12779(6)	1810(3)	124(7)
C(11)	1426(4)	11942(6)	1235(2)	89(5)
C(12)	2217(4)	12081(8)	1925(3)	135(7)
C(13)	-703(4)	8476(7)	2006(3)	117(6)
C(14)	-1190(4)	6653(7)	1808(3)	128(7)
C(15)	-28(3)	7010(6)	1937(2)	88(5)
C(16)	-1925(4)	8526(7)	1362(3)	124(7)
C(17)	-1922(3)	6997(6)	897(3)	110(6)
C(18)	-1611(3)	8834(6)	736(2)	85(5)
C(19)	-555(4)	6734(6)	-84(2)	92(5)
C(20)	-1630(3)	7222(7)	1(2)	103(5)
C(21)	-731(4)	8535(5)	117(2)	83(4)
C(22)	-1146(4)	5208(6)	401(2)	99(5)
C(23)	54(3)	5445(6)	620(3)	89(5)
C(24)	-560(3)	5564(5)	1131(2)	78(4)
C(25)	2541(3)	9913(6)	1406(2)	88(5)
C(26)	3167(3)	8831(7)	1040(3)	100(5)
C(27)	2745(3)	7976(6)	1557(2)	83(4)
C(28)	2089(4)	10217(6)	529(2)	94(5)
C(29)	2253(4)	8432(7)	242(3)	107(6)
C(30)	1151(3)	9102(6)	220(2)	72(4)
C(31)	1131(4)	5246(6)	1467(3)	110(6)
C(32)	2347(4)	5406(7)	1618(3)	114(6)
C(33)	1708(4)	6686(6)	1891(2)	87(5)
C(34)	1597(4)	4888(5)	763(3)	93(5)
C(35)	2479(3)	6213(7)	801(3)	97(5)
C(36)	1336(3)	6558(6)	372(2)	81(4)
N(1)	797(2)	9902(3)	1087(1)	41(2)
N(2)	415(2)	9306(3)	1574(1)	49(3)
N(3)	42(2)	11171(4)	1316(1)	53(3)
N(4)	1254(2)	10834(4)	1789(1)	54(3)
N(5)	-215(2)	8850(3)	910(1)	44(2)
N(6)	288(2)	7471(3)	1267(1)	46(2)
N(7)	-873(2)	7774(4)	1296(2)	55(3)
N(8)	-645(2)	7015(4)	620(2)	51(3)
N(9)	1348(2)	8409(3)	1432(1)	48(2)
N(10)	766(2)	8100(3)	790(1)	44(2)
N(11)	1615(2)	6655(4)	1119(1)	42(3)
N(12)	1968(2)	8559(4)	902(1)	47(2)
Si(1)	-207(1)	11713(2)	924(1)	70(1)
Si(2)	-335(1)	11343(2)	1597(1)	74(1)
Si(3)	1561(1)	10428(2)	2196(1)	79(1)
Si(4)	1491(1)	11858(2)	1698(1)	81(1)
Si(5)	-714(1)	7498(2)	1728(1)	81(1)
Si(6)	-1545(1)	8007(2)	1087(1)	78(1)

Table A-3 (continued)

Si(7)	-882(1)	7349(2)	195(1)	71(1)
Si(8)	-582(1)	5872(2)	685(1)	66(1)
Si(9)	2572(1)	8808(2)	1212(1)	66(1)
Si(10)	1874(1)	9031(2)	502(1)	65(1)
Si(11)	1697(1)	6047(2)	1496(1)	74(1)
Si(12)	1756(1)	6101(2)	788(1)	70(1)
Al(1)	567(1)	8673(1)	1178(1)	42(1)
Al(2)	633(1)	10442(2)	1465(1)	47(1)
Al(3)	-440(1)	7702(1)	1012(1)	48(1)
Al(4)	1497(1)	7860(2)	1051(1)	46(1)
C(1')	1182(6)	4503(11)	2571(4)	180
C(2')	648(7)	4443(12)	2474(4)	180
C(3')	261(5)	4364(10)	2592(5)	180

\* Equivalent isotropic U defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor

TABLE A-4  
MASS SPECTRUM OF  
 $\text{AlCl}_2\text{N}(\text{SiMe}_3)_2 \cdot \text{NEt}_3$

m/e	%	m/e	%	m/e	%	m/e	%
26	6.8	56	20.8	99	7.6	154	11.7
27	25.4	57	19.8	100	44.5	156	8.6
28	23.9	58	39.1	101	38.1	161	20.3
29	29.9	59	19.0	102	12.9	162	6.4
30	32.5	60	4.9	104	3.5	163	3.6
31	6.8	63	4.6	113	7.6	166	5.3
35	5.7	65	22.6	114	9.7	168	4.7
36	18.7	66	7.9	115	7.9	169	14.8
38	7.3	70	16.6	116	14.8	170	4.0
39	6.3	71	9.3	117	6.1	171	10.7
40	3.0	72	17.2	118	3.1	173	4.1
41	12.0	73	27.0	130	41.3	197	7.7
42	26.9	74	11.4	131	13.1	198	12.4
43	21.1	75	8.0	132	11.0	199	7.0
44	29.1	77	4.7	134	3.4	200	8.9
45	21.3	84	3.9	138	3.0	242	4.7
46	4.8	85	6.5	146	<u>100.0</u>	244	3.2
47	3.2	86	89.9	147	35.6	272	3.0
51	8.2	87	16.9	148	22.3	343	<3.0
52	4.0	93	13.9	149	6.5	359	3.1
54	5.5	95	6.2	150	6.3		
55	5.9	97	6.7	153	3.3		

Peaks having intensities lower than 3% of the base peak and lower than m/e 26 are not reported.

TABLE A-5  
MASS SPECTRUM OF  $\text{AlCl}[\text{N}(\text{SiMe}_3)_2]_2$

m/e	%	m/e	%	m/e	%	m/e	%
73	51.0	147	30.0	208	4.1	295	3.3
74	13.9	148	17.0	227	4.3	331	5.3
75	3.7	150	4.4	229	4.6	347	68.5
77	4.9	157	5.2	242	3.0	348	30.2
84	3.4	161	11.9	243	8.5	349	21.0
85	4.1	170	4.6	245	8.6	350	5.7
86	9.8	171	6.6	259	38.7	351	24.8
100	26.6	172	3.9	260	14.9	352	10.4
101	5.7	173	3.0	261	13.0	353	6.8
102	5.0	186	17.5	263	5.3	366	3.0
113	7.1	187	23.2	275	<u>100.0</u>	367	44.5
114	15.3	188	8.2	276	54.6	368	19.5
115	6.4	189	4.0	277	36.6	369	27.6
116	12.0	190	3.1	278	11.7	370	9.1
130	60.5	202	5.4	279	18.5	371	5.5
131	19.4	203	7.7	280	5.3	382	6.7M <sup>+</sup>
132	11.4	206	9.5	281	7.2	384	3.4
146	89.3	207	3.2	291	3.3		

Peaks having intensities lower than 3% of the base peak and lower than m/e 75 are not reported.

TABLE A-6  
MASS SPECTRUM OF  
 $\text{Al}[\text{N}(\text{SiMe}_3)_2]_3$

m/e	%	m/e	%	m/e	%	m/e	%
73	79.0	187	15.7	276	29.4	349	14.0
74	21.7	188	8.3	277	21.7	388	11.2
75	20.3	202	<u>100.0</u>	278	5.8	389	5.1
77	5.9	203	40.7	291	15.2	404	33.6
100	15.2	204	20.1	292	5.5	405	18.5
114	10.8	205	5.2	300	6.1	406	11.5
116	6.3	218	8.9	315	10.8	476	5.1
130	62.2	219	6.2	316	10.6	492	68.4
131	16.4	227	5.0	317	6.9	493	42.1
132	9.1	243	8.3	331	65.9	494	27.7
146	49.5	244	6.7	332	32.7	495	13.2
147	13.4	245	6.4	333	21.2	496	6.4
148	6.3	259	22.9	334	6.6	507	9.2M <sup>+</sup>
171	5.4	260	9.4	346	27.7	508	5.2
172	14.3	261	10.0	347	47.2		
186	16.3	275	70.2	348	23.9		

Peaks having intensities lower than 5% of the base peak and lower than m/e 73 are not reported.

TABLE A-7  
MASS SPECTRUM OF  $[\text{Me}_3\text{SiN}\cdot\text{AlN}(\text{SiMe}_3)_2]_2$

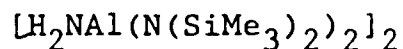
m/e	%	m/e	%	m/e	%	m/e	%
73	48.9	245	5.5	373	11.7	518	6.3
74	37.8	259	36.4	374	6.1	519	5.8
100	11.1	260	26.8	388	5.4	533	<u>100.0</u>
114	6.8	261	9.2	389	6.0	534	70.7
130	32.3	275	8.8	397	6.1	535	56.7
131	7.2	284	6.0	429	8.7	536	28.5
146	58.7	300	6.8	431	5.1	537	15.4
147	13.9	301	5.0	445	24.2	538	6.1
148	8.5	316	6.3	446	13.2	548	20.4M <sup>+</sup>
161	6.2	325	5.2	447	9.2	549	12.2
187	11.8	341	9.0	461	22.0	550	15.8
203	6.0	348	5.6	462	15.4	551	11.4
227	5.3	357	8.5	463	9.7	552	6.5
243	7.2	358	5.5	503	5.1		
244	5.0	372	7.7	517	11.0		

Peaks having intensities lower than 5% of the base peak and lower than m/e 73 are not reported.



TABLE A-8

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF



m/e	%	m/e	%	m/e	%	m/e	%
73	53.4	205	3.5	332	24.7	517	4.2
74	22.3	207	3.1	333	16.0	518	5.8
75	7.1	219	3.2	334	8.2	519	3.4
77	7.7	227	3.8	335	3.2	533	10.6
86	7.1	228	3.4	346	4.4	534	12.5
100	15.0	229	3.2	347	7.7	535	8.4
101	3.8	243	9.9	348	53.3	536	8.4
102	3.4	244	10.5	349	23.5	537	4.5
113	3.9	245	9.1	350	12.7	538	3.1
114	6.6	246	4.0	351	5.1	550	100.0
115	8.1	259	60.9	362	5.8	551	68.1
116	7.9	260	38.1	372	3.3	552	44.0
130	44.4	261	20.7	373	5.4	553	19.2
131	39.3	262	6.6	374	4.6	554	9.3
132	11.6	273	5.2	375	3.8	565	19.8
146	66.6	274	4.9	388	7.3	566	48.7
147	22.7	275	50.8	389	22.3	567	29.5
148	11.6	276	24.6	390	9.3	568	19.4
150	4.5	277	16.6	391	7.7	569	7.3
161	7.5	278	4.0	404	3.1	570	4.4
171	5.5	291	7.6	405	15.1	711	28.0
172	3.9	292	4.1	406	7.5	712	22.0
173	3.8	300	6.7	407	4.1	713	17.8
186	6.5	301	5.5	445	5.2	714	8.9
187	21.4	302	4.6	446	3.6	715	4.7
188	9.0	315	3.9	461	6.0	726	9.0
189	6.3	316	15.2	462	7.2	727	6.3
202	5.9	317	9.4	463	3.8	728	4.7
203	30.4	318	6.4	493	9.0		
204	8.9	331	7.9	494	4.7		

Peaks having intensities lower than 3% of the base peak and lower than m/e 73 are not reported.

TABLE A-9

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF  
THE PRODUCTS OF  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{AlCl}$  WITH AMMONIA AT  $-20^\circ\text{C}$

m/e	%	m/e	%	m/e	%	m/e	%
28	14.5	153	5.1	261	25.1	372	8.2
31	5.6	161	5.2	262	10.3	373	12.5
43	8.4	170	6.1	273	4.4	374	6.2
45	13.0	171	11.5	275	41.3	375	6.9
57	10.8	172	9.2	276	30.1	388	12.1
59	11.2	173	9.3	277	14.7	389	25.9
65	7.6	174	16.2	284	5.5	390	12.6
73	51.9	175	5.0	289	6.0	391	6.9
74	20.0	186	12.8	290	10.2	405	93.2
75	5.1	187	40.3	291	37.6	406	48.5
77	5.6	188	15.3	292	18.5	407	34.1
85	6.8	189	10.0	293	11.3	408	12.8
86	6.8	202	10.8	300	10.3	409	5.1
100	16.8	203	76.9	301	7.0	420	5.2
101	15.4	204	25.0	302	5.1	421	6.7
103	6.8	205	11.2	316	20.0	461	8.3
114	11.9	217	6.7	317	14.9	550	8.8
115	15.0	218	5.4	318	8.1	551	4.8
116	10.0	227	6.3	331	6.7	566	100.0
130	44.6	228	8.2	332	24.3	567	73.9
131	23.4	229	5.6	333	12.3	568	52.8
132	11.0	243	13.9	334	7.1	569	26.2
146	47.5	244	16.5	347	12.0	570	14.1
147	16.0	245	12.2	348	83.4	571	5.1
148	7.8	246	6.8	349	39.8		
150	5.6	259	59.3	350	29.9		
151	8.9	260	56.2	351	7.4		

Peaks having intensities lower than 5% of the base peak and lower than m/e 28 are not reported.